Chemical Wisdom- Horse Chestnuts and the Fermentation of Powerful Powders

Nitrocellulose, Guncotton, Cordite, Nitrogylcerine, Ballistite, Smokeless Powder, Acetone, Poudre B, Acetone-butanol-ethanol fermentation, Horse Chestnut.

cellulose nitrate, **flash paper**, **flash cotton**, **flash string** is a highly flammable compound formed by nitrating cellulose through exposure to nitric acid or another powerful nitrating agent. When used as a propellant or low-order explosive, it was originally known as **guncotton**. Nitrocellulose plasticized by camphor was used by Kodak, and other suppliers, from the late 1880s as a film base in photograph, X-ray films and motion picture films; and was known as *nitrate film*. After numerous fires caused by unstable nitrate films, safety film started to be used from the 1930s in the case of X-ray stock and from 1948 for motion picture film.

Guncotton

Pure nitrocellulose

Various types of smokeless powder, consisting primarily of nitrocellulose

Henri Braconnot discovered in 1832 that nitric acid, when combined with starch or wood fibers, would produce a lightweight combustible explosive material, which he named *xyloïdine*. A few years later in 1838 another French chemist Théophile-Jules Pelouze (teacher of Ascanio Sobrero and Alfred Nobel) treated paper and cardboard in the same way. He obtained a similar material he called *nitramidine*. Both of these substances were highly unstable, and were not practical explosives.

However, around 1846 Christian Friedrich Schönbein, a German-Swiss chemist, discovered a more practical solution. As he was working in the kitchen of his home in Basel, he spilled a bottle of concentrated nitric acid on the kitchen table. He reached for the nearest cloth, a cotton apron, and wiped it up. He hung the apron on the stove door to dry, and, as soon as it was dry, there was a flash as the apron exploded. His preparation method was the first to be widely imitated—one part of fine cotton wool to be immersed in fifteen parts of an equal blend of sulfuric and nitric acids. After two minutes, the cotton was removed and washed in cold water to set the esterification level and remove all acid residue. It was then slowly dried at a temperature below 100 °F (about 38 °C). Schönbein collaborated with the Frankfurt professor Rudolf Christian Böttger, who had discovered the process independently in the same year. By coincidence, a third chemist, the Brunswick professor F. J. Otto had also produced guncotton in 1846 and was the first to publish the process, much to the disappointment of Schönbein and Böttger.[2]

The process uses nitric acid to convert cellulose into cellulose nitrate and water:

$$3HNO_3 + C_6H_{10}O_5 \rightarrow C_6H_7(NO_2)_3O_5 + 3H_2O$$

The sulfuric acid is present as a catalyst to produce the nitronium ion, NO_2^+. The reaction is first order and proceeds by electrophilic substitution at the C-OH centers of the cellulose.[3]

The power of guncotton made it suitable for blasting. As a projectile driver, it has around six times the gas generation of an equal volume of black powder and produces less smoke and less heating. However, the sensitivity of the material during production led the British, Prussians and French to discontinue manufacture within a year.

Jules Verne viewed the development of guncotton with optimism. He referred to the substance several times in his novels. His adventurers carried firearms employing this substance. The most noteworthy reference is in his *From the Earth to the Moon*, in which guncotton was used to launch a projectile into space.

Further research indicated the importance of very careful washing of the acidified cotton. Unwashed nitrocellulose (sometimes called *pyrocellulose*) may spontaneously ignite and explode at room temperature, as the evaporation of water results in the concentration of unreacted acid.[4] The British, led by Frederick Augustus Abel, developed a much lengthier manufacturing process at the Waltham Abbey Royal Gunpowder Mills, patented in 1865, with the washing and drying times each extended to 48 hours and repeated eight times over. The acid mixture was changed to two parts sulfuric acid to one part nitric. Nitration can be controlled by adjusting acid concentrations and reaction temperature. Nitrocellulose is soluble in a mixture of alcohol and ether until nitrogen concentration exceeds 12 percent. Soluble nitrocellulose, or a solution thereof, is sometimes called *collodion*.[5]

Guncotton containing more than 13 percent nitrogen (sometimes called *insoluble nitrocellulose*) was prepared by prolonged exposure to hot, concentrated acids[5] for limited use as a blasting explosive or for warheads of underwater weapons like naval mines and torpedoes.[4] Guncotton, dissolved at approximately 25% in acetone, forms a lacquer used in preliminary stages of wood finishing to develop a hard finish with a deep lustre.[*citation needed*] It is normally the first coat applied, sanded and followed by other coatings that bond to it.

More stable and slower burning collodion mixtures were eventually prepared using less concentrated acids at lower temperatures for smokeless powder in firearms. The first practical smokeless powder made from nitrocellulose, for firearms and artillery ammunition, was invented by French chemist Paul Vieille in 1884.

Nitrate film

Nitrocellulose was used as the first flexible film base, beginning with Eastman Kodak products in August, 1889. Camphor is used as a plasticizer for nitrocellulose film, often called nitrate film. It was used until 1933 for X-ray films (where its flammability hazard was most acute) and for motion picture film until 1951. It was replaced by safety film with an acetate base.

The use of nitrocellulose film for motion pictures led to the requirement for fireproof projection rooms with wall coverings made of asbestos. The US Navy shot a training film for projectionists that included footage of a controlled ignition of a reel of nitrate film, which continued to burn when fully submerged in water. Unlike many other flammable materials, nitrocellulose does not need air to keep burning as the reaction produces oxygen. Once burning, it is extremely difficult to extinguish. Immersing burning film in water may not extinguish it, and could actually increase the amount of smoke produced.[6][7] Owing to public safety precautions, the London Underground forbade transport of movies on its system until well past the introduction of safety film.

Cinema fires caused by ignition of nitrocellulose film stock were the cause of the 1926 Dromcolliher cinema tragedy in County Limerick in which 48 people died and the 1929 Glen Cinema Disaster in Paisley, Scotland which killed 69 children. Today, nitrate film projection is normally highly regulated and requires extensive precautionary measures including extra projectionist health and safety training. Projectors certified to run nitrate films have many precautions, among them the chambering of the feed and takeup reels in thick metal covers with small slits to allow the film to run through. The projector is modified to accommodate several fire extinguishers with nozzles aimed at the film gate. The extinguishers automatically trigger if a piece of flammable fabric placed near the gate starts to burn. While this triggering would likely damage or destroy a significant portion of the projection components, it would prevent a fire which could cause far greater damage. Projection rooms may be required to have automatic metal covers for the projection windows, preventing the spread of fire to the auditorium.

Nitrocellulose film on a light box, showing deterioration. From Library and Archives Canada collection.

It was found that nitrocellulose gradually decomposes, releasing nitric acid and further catalyzing the decomposition (eventually into a flammable powder). Decades later, storage at low temperatures was discovered as a means of delaying these reactions indefinitely. It is thought that the great majority of films produced during the early twentieth century were lost either through this accelerating, self-catalyzed disintegration or through studio warehouse fires. Salvaging old films is a major problem for film archivists (see film preservation).

Nitrocellulose film base manufactured by Kodak can be identified by the presence of the word *Nitrate* in dark letters between the perforations. Acetate film manufactured during the era when nitrate films were still in use was marked *Safety* or *Safety Film* between the perforations in dark letters. Film stocks in smaller gauges intended for non-theatrical or amateur use, 8 mm, 16 mm, and others, were not manufactured with a nitrate base on any significant scale in the west, though rumours persist of 16mm nitrate having been produced in the former Soviet Union and/or China.[8]

Production

Guncotton

In general, cotton was used as the cellulose base, and is added to concentrated sulfuric acid and 70% nitric acid cooled to 0 °C to give cellulose trinitrate (or *guncotton*).

While guncotton is dangerous to store, its risks can be reduced by storing it wet or in oil.

Nitrate film

Cellulose is treated with sulfuric acid and potassium nitrate to give cellulose mononitrate. This was used commercially as *Celluloid*, a highly flammable plastic used in the first half of the 20th Century for lacquers and photographic film.[11]

Uses

An M13 rocket for the Katyusha launcher on display in the Musée de l'Armée. Its solid-fuel rocket motor was prepared from nitrocellulose.

- A nitrocellulose slide, nitrocellulose membrane or nitrocellulose paper is a sticky membrane used for immobilizing nucleic acids in Southern blots and northern blots. It is also used for immobilization of proteins in Western blots and Atomic Force Microscopy[12] for its non-specific affinity for amino acids. Nitrocellulose is widely used as support in diagnostic tests where antigen-antibody binding occur, e.g., pregnancy tests, U-Albumin tests and CRP. Glycine and chloride ions make protein transfer more efficient.

- When the solution is dissolved in ether, alcohol or other organic solvents it produces collodion, discovered in 1846 and introduced as a wound dressing during the Crimean War. It is still in use today in topical skin applications, such as liquid skin and in the application of salicylic acid, the active ingredient in *Compound W* wart remover.
- Adolph Noé developed a method of peeling coal balls using nitrocellulose.[13]
- In 1851, Frederick Scott Archer invented the Wet Collodion Process as a replacement for albumen in early photographic emulsions, binding light-sensitive silver halides to a glass plate.[14]
- Magician's flash paper, sheets of paper or cloth made from nitrocellulose, which burn almost instantly with a bright flash leaving no ash.
- Radon tests for alpha track etches.
- Space flight, nitrocellulose is used by Copenhagen Suborbitals as a means of jettisoning space-craft components like their protection lid.
- Nitrocellulose lacquer was used as a finish on guitars and saxophones for most of the 20th century and is still used on some current applications. Manufactured by (among others) DuPont, the paint was also used on automobiles sharing the same color codes as many guitars including Fender and Gibson brands,[15] although it fell out of favor for a number of reasons: pollution, and the way the lacquer yellows and cracks over time.
- Nitrocellulose lacquer is also used as an aircraft dope, painted onto fabric-covered aircraft to tauten and provide protection to the material.
- It is also used to coat playing cards and to hold staples together in office staplers.
- As a medium for cryptographic one-time pads, thus making the disposal of the pad complete, secure, and efficient.
- Nitrocellulose lacquer is spin-coated onto aluminum or glass discs, then a groove is cut with a lathe, to make one-off phonograph records, used as masters for pressing or for play in dance clubs. They are referred to as acetate discs.
- Depending on the manufacturing process, nitrocellulose is esterified to varying degrees. Table tennis balls, guitar picks and some photographic films have a fairly low esterification level and burn comparatively slowly with some charred residue. See celluloid.

Because of its explosive nature, not all applications of nitrocellulose were successful. In 1869, with elephants having been poached to near extinction, the billiards industry offered a $10,000 prize to whoever came up with the best replacement for ivory billiard balls. John Wesley Hyatt created the winning replacement, which he created with a new material he discovered called camphored nitrocellulose—the first thermoplastic, better known as celluloid. The invention enjoyed a brief popularity, but the Hyatt balls were extremely flammable, and sometimes portions of the outer shell would explode upon impact. An owner of a billiard saloon in Colorado wrote to Hyatt about the explosive tendencies, saying that he did not mind very much personally but for the fact that every man in his saloon immediately pulled a gun at the sound.[16][17] The process used by Hyatt to manufacture the billiard balls (US Patent 239,792, 1881) involved placing the mass of nitrocellulose in a rubber bag, which was then placed in a cylinder of liquid and heated. Pressure was applied to the liquid in the cylinder, which resulted in a uniform compression on the nitrocellulose mass, compressing it into a uniform sphere as the heat vaporized the solvents. The ball was then cooled and turned to make a uniform sphere. In light of the explosive results, this process was called the "Hyatt Gun Method".[18]

References

1. ^ *Merck Index*, 11th Edition, **8022**.
2. ^ Itzehoer Wochenblatt, 29 October 1846, columns 1626 f.
3. ^ Urbanski, Tadeusz, *Chemistry and Technology of Explosives*, Pergamon Press, Oxford, 1965, Vol 1, pp 20–21.
4. ^ a b Fairfield, A. P., CDR USN. *Naval Ordnance*. Lord Baltimore Press (1921) pages 28–31.
5. ^ a b Brown, G.I. (1998). *The Big Bang: A history of Explosives*. Sutton Publishing p.132 ISBN 0-7509-1878-0
6. ^ Health and Safety Executive leaflet/cellulose.pdf
7. ^ [*dead link*]Interesting discussion on NC films.
8. ^ David Cleveland, "Don't Try This at Home: Some Thoughts on Nitrate Film, With Particular Reference to Home Movie Systems" in Roger Smither and Catherine Surowiec (eds.), *This Film is Dangerous: A Celebration of Nitrate Film*, Brussels, FIAF (2002), ISBN 978-2-9600296-0-4, p. 196
9. ^ Charles Fordyce et al., "Improved Safety Motion Picture Film Support", *Journal of the SMPE*, vol. 51 (October 1948), pp. 331–350
10. ^ George J. van Schil, 'The Use of Polyester Film Base in the Motion Picture Industry', SMPTE Journal, vol. 89, no. 2 (February 1980), pp. 106–110.
11. ^ http://fliiby.com/file/208138/a7bake2p2k.html
12. ^ L. Kreplak et al. Atomic Force Microscopy of Mammalian Urothelial Surface. Journal of molecular biology. Volume 374, Issue 2, 23 November 2007, Pages 365-373
13. ^ Kraus, E. J. (September 1939). "Adolf Carl Noe". *Botanical Gazette* (University of Chicago Press) **101** (1): 231. doi:10.1086/334861. JSTOR 2472034.
14. ^ Dr. R Leggat, A History of Photography: The Collodion Process
15. ^ "What is "stand damage"?".
16. ^ Connections, James Burke, Volume 9, "Countdown", 29:00 – 31:45, 1978
17. ^ United States. National Resources Committee (1941). *RESEARCH—A NATIONAL RESOURCE*. UNITED STATES GOVERNMENT PRINTING OFFICE. p. 29.
18. ^ Edward Chauncey Worden (1911). *Nitrocellulose Industry, Volume 2*. D. Van Nostrand Company. pp. 726–727.

Acetone

Acetone (systematically named **propanone**) is the organic compound with the formula $(CH_3)_2CO$. It is a colorless, mobile, flammable liquid, and is the simplest ketone.

Acetone is miscible with water and serves as an important solvent in its own right, typically for cleaning purposes in the laboratory. About 6.7 million tonnes were produced worldwide in 2010, mainly for use as a solvent and production of methyl methacrylate and bisphenol A.[7][8] It is a common building block in organic chemistry. Familiar household uses of acetone are as the active ingredient in nail polish remover and as paint thinner.

Acetone is produced and disposed of in the human body through normal metabolic processes. It is normally present in blood and urine. People with diabetes produce it in larger amounts. Reproductive toxicity tests show that it has low potential to cause reproductive problems. Pregnant women nursing mothers and children have higher levels of acetone.[*citation needed*] Ketogenic diets that increase acetone in the body are used to reduce epileptic attacks in infants and children who suffer from recalcitrant refractory epilepsy.

Biosynthesis

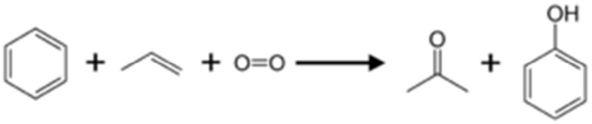
Small amounts of acetone are produced in the body by the decarboxylation of ketone bodies. Certain dietary patterns, including prolonged fasting and high-fat low-carbohydrate dieting, can produce ketosis, in which acetone is formed in body tissue, and certain health conditions, such as alcoholism and diabetes, can produce ketoacidosis, uncontrollable ketosis that leads to a sharp, and potentially fatal, increase in the acidity of the blood. Since it is a byproduct of fermentation, acetone is a byproduct of the distillery industry.

Production

In 2010, the worldwide production capacity for acetone was estimated at 6.7 million tonnes per year.[9] With 1.56 million tonnes per year, the United States had the highest production capacity,[10] followed by Taiwan and mainland China. The largest producer of acetone is INEOS Phenol, owning 17% of the world's capacity, with also significant capacity (7–8%) by Mitsui, Sunoco and Shell in 2010.[9] INEOS Phenol also owns the world's largest production site (420,000 tonnes/annum) in Beveren (Belgium). Spot price of acetone in summer 2011 was 1100–1250 USD/tonne in the United States.[11]

Current method

Acetone is produced directly or indirectly from propylene. Approximately 83% of acetone is produced via the cumene process,[8] as a result, acetone production is tied to phenol production. In the cumene process, benzene is alkylated with propylene to produce cumene, which is oxidized by air to produce phenol and acetone:



Other processes involve the direct oxidation of propylene (Wacker-Hoechst process), or the hydration of propylene to give 2-propanol, which is oxidized to acetone.[8]

Older methods

Previously, acetone was produced by the dry distillation of acetates, for example calcium acetate in ketonic decarboxylation.

$$Ca(CH_3COO)_2 \rightarrow CaO(s) + CO_2(g) + (CH_3)_2CO(v)$$

Before that, during World War I acetone was produced using acetone-butanol-ethanol fermentation with *Clostridium acetobutylicum* bacteria, which was developed by Chaim Weizmann (later the first president of Israel) in order to help the British war effort[8] in the preparation of Cordite.[12] This acetone-butanol-ethanol fermentation was eventually abandoned when newer methods with better yields were found.[8]

Uses

About a third of the world's acetone is used as a solvent, and a quarter is consumed as acetone cyanohydrin a precursor to methyl methacrylate.[7]

[] Solvent

Acetone is a good solvent for many plastics and some synthetic fibers. It is used for thinning polyester resin, cleaning tools used with it, and dissolving two-part epoxies and superglue before they harden. It is used as one of the volatile components of some paints and varnishes. As a heavy-duty degreaser, it is useful in the preparation of metal prior to painting. It is also useful for high reliability soldering applications to remove rosin flux after soldering is complete; this helps to prevent the Rusty bolt effect.

Acetone is used as a solvent by the pharmaceutical industry and as a denaturant in denatured alcohol.[13] Acetone is also present as an excipient in some pharmaceutical drugs.[14]

Although itself flammable, acetone is used extensively as a solvent for the safe transporting and storing of acetylene, which cannot be safely pressurized as a pure compound. Vessels containing a porous material are first filled with acetone followed by acetylene, which dissolves into the acetone. One liter of acetone can dissolve around 250 liters of acetylene.[15][16]

[] Chemical intermediate

Acetone is used to synthesize methyl methacrylate. It begins with the initial conversion of acetone to acetone cyanohydrin:

$$(CH_3)_2CO + HCN \rightarrow (CH_3)_2C(OH)CN$$

In a subsequent step, the nitrile is hydrolyzed to the unsaturated amide, which is esterified:

$$(CH_3)_2C(OH)CN + CH_3OH \rightarrow CH_2{=}(CH_3)CCO_2CH_3 + NH_3$$

The third major use of acetone (about 20%)[7] is synthesizing bisphenol A. Bisphenol A is a component of many polymers such as polycarbonates, polyurethanes, and epoxy resins. The synthesis involves the condensation of acetone with phenol:

$$(CH_3)_2CO + 2\ C_6H_5OH \rightarrow (CH_3)_2C(C_6H_4OH)_2 + H_2O$$

Many millions of kilograms of acetone are consumed in the production of the solvents methyl isobutyl alcohol and methyl isobutyl ketone. These products arise via an initial aldol condensation to give diacetone alcohol.[8]

$$2\ (CH_3)_2CO \rightarrow (CH_3)_2C(OH)CH_2C(O)CH_3$$

[] Laboratory

In the laboratory, acetone is used as a polar, aprotic solvent in a variety of organic reactions, such as S_N2 reactions. The use of acetone solvent is critical for the Jones oxidation. It does not form an azeotrope with water (see azeotrope (data)).[17] It is a common solvent for rinsing laboratory glassware because of its low cost and volatility. Despite its common use as a supposed drying agent, it is not effective except by bulk displacement and dilution. Acetone can be cooled with dry ice to −78 °C without freezing; acetone/dry ice baths are commonly used to conduct reactions at low temperatures. Acetone is fluorescent under ultraviolet light, and its vapor may be used as a fluorescent tracer in fluid flow experiments.[18]

[] Medical and cosmetic uses

Acetone is used in a variety of general medical and cosmetic applications and is also listed as a component in food additives and food packaging. Dermatologists use acetone with alcohol for acne treatments to peel dry skin.

Acetone is commonly used in chemical peeling. Common agents used today for chemical peels are salicylic acid, glycolic acid, 30% salicylic acid in ethanol, and trichloroacetic acid (TCA). Prior to chemexfoliation, the skin is cleaned and excess fat removed in a process called defatting. Acetone, Septisol, or a combination of these agents is commonly used in this process.[*citation needed*]

[] Domestic and other niche uses

Acetone is often the primary component in cleaning agents such as nail polish remover. Acetone is a component of superglue remover and easily removes residues from glass and porcelain. Make-up artists use acetone to remove skin adhesive from the netting of wigs and moustaches by immersing the item in an acetone bath, then removing the softened glue residue with a stiff brush.

This chemical is also used as an artistic agent; when rubbed on the back of a laser print or photocopy placed face-down on another surface and burnished firmly, the toner of the image transfers to the destination surface.[*citation needed*]

Acetone can also be used in combination with automatic transmission fluid to create an effective penetrating oil. Brake fluid is sometimes used in place of ATF. These mixtures (usually 1:1) can be useful in loosening rusted or stuck bolts.[*citation needed*]

Safety

Flammability

The most hazardous property of acetone is its extreme flammability. At temperatures greater than acetone's flash point of −20 °C (−4 °F), air mixtures of between 2.5% and 12.8% acetone, by volume, may explode or cause a flash fire. Vapors can flow along surfaces to distant ignition sources and flash back. Static discharge may also ignite acetone vapors. Acetone has, however very high ignition initiation energy point, so accidental ignition is rare. Even pouring or spraying acetone over red-glowing coal will not ignite it, due to the high concentration of vapour and the cooling effect of evaporation of the liquid.[19] It auto-ignites at 465 °C (869 °F). Autoignition temperature is also dependent upon the exposure time, thus at some tests it is quoted as 525°C. Also, industrial acetone is likely to contain small amount of water which also inhibits ignition.

Acetone peroxide

Main article: acetone peroxide

When oxidized, acetone forms acetone peroxide as a byproduct, which is a highly unstable compound. It may be formed accidentally, e.g. when waste hydrogen peroxide is poured into waste solvent containing acetone. Due to its instability, it is rarely used, despite its easy chemical synthesis.

Health information

Acetone has been studied extensively and is generally recognized to have low acute and chronic toxicity if ingested and/or inhaled. Inhalation of high concentrations (around 9200 ppm) in the air caused irritation of the throat in humans in as little as 5 minutes. Inhalation of concentrations of 1000 ppm caused irritation of the eyes and of the throat in less than 1 hour; however, the inhalation of 500 ppm of acetone in the air caused no symptoms of irritation in humans even after 2 hours of exposure. Acetone is not currently regarded as a carcinogen, a mutagenic chemical or a concern for chronic neurotoxicity effects.[19]

Acetone can be found as an ingredient in a variety of consumer products ranging from cosmetics to processed and unprocessed foods. Acetone has been rated as a GRAS (Generally Recognized as Safe) substance when present in beverages, baked foods, desserts, and preserves at concentrations ranging from 5 to 8 mg/L. Additionally, a joint U.S-European study found that acetone's "health hazards are slight."[*citation needed*]

Toxicology

Acetone is believed to exhibit only slight toxicity in normal use, and there is no strong evidence of chronic health effects if basic precautions are followed.[20]

At very high vapor concentrations, acetone is irritating and, like many other solvents, may depress the central nervous system. It is also a severe irritant on contact with eyes, and a potential pulmonary aspiration risk. In one documented case, ingestion of a substantial amount of acetone led to systemic toxicity, although the patient eventually fully recovered.[21] Some sources estimate LD_{50} for human ingestion at 1.159 g/kg; LD_{50} inhalation by mice is given as 44 g/m^3, over 4 hours.[22]

Acetone has been shown to have anticonvulsant effects in animal models of epilepsy, in the absence of toxicity, when administered in millimolar concentrations.[23] It has been hypothesized that the high-fat low-carbohydrate ketogenic diet used clinically to control drug-resistant epilepsy in children works by elevating acetone in the brain.[23]

- EPA EPCRA Delisting (1995). EPA removed acetone from the list of "toxic chemicals" maintained under Section 313 of the Emergency Planning and Community Right to Know Act (EPCRA). In making that decision, EPA conducted an extensive review of the available toxicity data on acetone and found that acetone "exhibits acute toxicity only at levels that greatly exceed releases and resultant exposures", and further that acetone "exhibits low toxicity in chronic studies".

- Genotoxicity. Acetone has been tested in more than two dozen in vitro and in vivo assays. These studies indicate that acetone is not genotoxic.

- Carcinogenicity. EPA in 1995 concluded, "There is currently no evidence to suggest a concern for carcinogenicity". (EPCRA Review, described in Section 3.3). NTP scientists have recommended against chronic toxicity/carcinogenicity testing of acetone because "the prechronic studies only demonstrated a very mild toxic response at very high doses in rodents".

- Neurotoxicity and Developmental Neurotoxicity. The neurotoxic potential of both acetone and isopropanol, the metabolic precursor of acetone, have been extensively studied. These studies demonstrate that although exposure to high doses of acetone may cause transient central nervous system effects, acetone is not a neurotoxicant. A guideline developmental neurotoxicity study has been conducted with isopropanol, and no developmental neurotoxic effects were identified, even at the highest dose tested. (SIAR, pp. 1, 25, 31).

- Environmental. When the EPA exempted acetone from regulation as a volatile organic compound (VOC) in 1995, EPA stated that this exemption would "contribute to the achievement of several important environmental goals and would support EPA's pollution prevention efforts". 60 Fed. Reg. 31,634 (June 16, 1995). 60 Fed. Reg. 31,634 (June 16, 1995). EPA noted that acetone could be used as a substitute for several compounds that are listed as hazardous air pollutants (HAP) under section 112 of the Clean Air Act.

Environmental effects

Acetone evaporates rapidly, even from water and soil. Once in the atmosphere, it has a 22-day half-life and is degraded by UV light via photolysis (primarily into methane and ethane[24]). Acetone dissipates slowly in soil, animals, or waterways since it is sometimes consumed by microorganisms,[25] but it is a significant groundwater contaminant due to its high solubility in water. The LD_{50} of acetone for fish is 8.3 g/L of water (or about 1%) over 96 hours, and its environmental half-life is about 1 to 10 days. Acetone may pose a significant risk of oxygen depletion in aquatic systems due to the microbial consumption.[26]

References

1. ^ *Merck Index*, 11th Edition, **58**
2. ^ "Acetone – PubChem Public Chemical Database". *The PubChem Project*. USA: National Center for Biotechnology Information.
3. ^ *a* *b* *c* "Acetone". *NIST Chemistry WebBook*. USA: National Institute of Standards and Technology.
4. ^ Klamt, Andreas (2005). *COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*. Elsevier. pp. 92–94. ISBN 978-0-444-51994-8.
5. ^ Ash, Michael; Ash, Irene (2004). *Handbook of preservatives*. Synapse Information Resources, Inc. p. 369. ISBN 1-890595-66-7.
6. ^ Myers, Richard L. (2007). *The 100 Most Important Chemical Compounds: A Reference Guide*. Greenwood. pp. 4–6. ISBN 978-0-313-08057-9.
7. ^ *a* *b* *c* Acetone, World Petrochemicals report, January 2010
8. ^ *a* *b* *c* *d* *e* *f* Stylianos Sifniades, Alan B. Levy, "Acetone" in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2005.
9. ^ *a* *b* Camara Greiner, EO and Funada, C (June 2010). "CEH Marketing Research Report: ACETONE". *Chemical Economics Handbook*. SRI consulting. Retrieved March 2011.
10. ^ "Acetone Uses and Market Data". ICIS.com. October 2010. Retrieved 2011-03-21.
11. ^ Acetone (US Gulf) Price Report – Chemical pricing information. ICIS Pricing. Retrieved on 2012-11-26.
12. ^ Wittcoff, M.M. Green ; H.A. (2003). *Organic chemistry principles and industrial practice* (1. ed., 1. reprint. ed.). Weinheim: Wiley-VCH. p. 4. ISBN 3-527-30289-1.
13. ^ Weiner, Myra L.; Lois A. Kotkoskie (1999). *Excipient Toxicity and Safety*. p. 32. ISBN 978-0-8247-8210-8.
14. ^ Inactive Ingredient Search for Approved Drug Products, FDA/Center for Drug Evaluation and Research
15. ^ Mine Safety and Health Administration (MSHA) – Safety Hazard Information – Special Hazards of Acetylene. Msha.gov. Retrieved on 2012-11-26.
16. ^ History – Acetylene dissolved in acetone. Aga.com. Retrieved on 2012-11-26.
17. ^ What is an Azeotrope?. Solvent—recycling.com. Retrieved on 2012-11-26.
18. ^ A. Lozano, B. Yip and R. K. Hanson (1992). "Acetone: a tracer for concentration measurements in gaseous flows by planar laser-induced fluorescence". *Exp. Fluids* **13** (6): 369–376. doi:10.1007/BF00223244.
19. ^ *a* *b* Acetone MSDS. Hazard.com (1998-04-21). Retrieved on 2012-11-26.
20. ^ Basic Information on Acetone. Ccohs.ca (1999-02-19). Retrieved on 2012-11-26.
21. ^ Canadian Centre for Occupational Health and Safety. "Health Effects of Acetone". Archived from the original on 17 October 2008. Retrieved 2008-10-21.

22. ^ Safety (MSDS) data for propanone. Msds.chem.ox.ac.uk. Retrieved on 2012-11-26.
23. ^ *a* *b* Likhodii SS, Serbanescu I, Cortez MA, Murphy P, Snead OC 3rd, Burnham WM (2003). "Anticonvulsant properties of acetone, a brain ketone elevated by the ketogenic diet". *Ann Neurol.* **54** (2): 219–226. doi:10.1002/ana.10634. PMID 12891674.
24. ^ Darwent, B. deB.; Allard, M. J.; Hartman, M. F.; Lange, L. J. (1960). "The Photolysis of Acetone". *Journal of Physical Chemistry* **64** (12): 1847. doi:10.1021/j100841a010.
25. ^ Acetone, Agency for Toxic Substances and Disease Registry ToxFAQs, 1995
26. ^ Safety Data Sheet Acetone. (PDF) . Retrieved on 2012-11-26.

Cordite

A stick of cordite from World War II.

A sectioned British 18 pounder field gun shrapnel round, World War I, showing string bound to roughly simulate the appearance of the cordite propellant

Sticks of cordite from a .303 British rifle cartridge.

Cordite is a family of smokeless propellants developed and produced in the United Kingdom from 1889 to replace gunpowder as a military propellant. Like gunpowder, cordite is classified as a low explosive because of its slow burning rates and consequently low brisance. These produce a subsonic deflagration wave rather than the supersonic detonation wave produced by brisants, or high explosives. The hot gases produced by burning gunpowder or cordite generate sufficient pressure to propel a bullet or shell to its target, but not so quickly as to routinely destroy the barrel of the firearm, or gun.

Cordite was used initially in the .303 British, Mark I and II, standard rifle cartridge between 1891 and 1915; shortages of cordite in World War I led to United States–developed smokeless powders being imported into the UK for use in rifle cartridges. Cordite was also used for large weapons, such as tank guns, artillery and naval guns. It has been used mainly for this purpose since the late 19th century by the UK and British Commonwealth countries. Its use was further developed before World War II, and as 2-and-3-inch-diameter (51 and 76 mm) Unrotated Projectiles for launching anti-aircraft weapons.[1] Small cordite rocket charges were also developed for ejector seats made by the Martin-Baker Company. Cordite was also used in the detonation system of the Little Boy atomic bomb dropped over Hiroshima in August 1945.

The term cordite generally disappeared from official publications between the wars. During World War II double based propellants were very widely used and there was some use of triple based propellants by artillery. Triple based propellants were used in post-war ammunition designs and remain in production for UK weapons; most double based propellants left service as World War II stocks were expended after the war. For small arms it has been replaced by other propellants, such as the Improved Military Rifle (IMR) line of extruded powder or the WC844 ball propellant currently in use in the 5.56×45mm NATO.[2] Production ceased in the United Kingdom, around the end of the 20th century, with the closure of the last of the World War II cordite factories, ROF Bishopton. Triple base propellant for UK service (for example, the 105 mm L118 Light Gun) is now manufactured in Germany.

Adoption of smokeless powder by the British government

Replacements for gunpowder (black powder)

Gunpowder, an explosive mixture of sulfur, charcoal and potassium nitrate (also known as saltpetre/saltpeter), was the original gun propellant employed in firearms and fireworks. It was used from about 10th or 11th century onwards, but it had disadvantages, including the large quantity of smoke it produced. With the 19th-century development of various "nitro explosives", based on the reaction of nitric acid mixtures on materials such as cellulose and glycerine, a search began for a replacement for gunpowder.

Early European smokeless powders

The first smokeless powder was developed in 1865 by Major Johann F. E. Schultze of the Prussian artillery. His formulation (dubbed **Schultze Powder**) comprised nitrolignose impregnated with saltpetre or barium nitrate.

In 1882 the Explosive Company of Stowmarket introduced **EC Powder**, which contained nitro-cotton and nitrates of potassium and barium in a grain gelatinesed by ether alcohol. It had coarser grains than other nitrocellulose powders. It proved unsuitable for rifles, but it remained in long use for shotguns[3] and was later used for grenades and fragmentation bombs.[4]

In 1884, the French chemist Paul Vieille produced a smokeless propellant that had some success. It was made out of collodion (nitrocellulose dissolved in ethanol and ether), resulting into a plastic colloidal substance which was rolled into very thin sheets, then dried and cut up into small flakes. It was immediately adopted by the French military for their Mle 1886 infantry rifle and called **Poudre B** (for *Poudre Blanche*, or "White Powder") to distinguish it from "Black Powder" (gunpowder). The rifle and the cartridge developed to use this powder were known generically as the 8mm Lebel, after the officer who developed its 8 mm full metal jacket bullet.

The following year, 1887, Alfred Nobel invented and patented a smokeless propellant he called **Ballistite**. It was composed of 10% camphor, 45% nitroglycerine and 45% collodion (nitrocellulose). Over time the camphor tended to evaporate, leaving an unstable explosive.

Development of Cordite

A United Kingdom government committee, known as the "Explosives Committee", chaired by Sir Frederick Abel, monitored foreign developments in explosives and obtained samples of Poudre B and Ballistite; neither of these smokeless powders was recommended for adoption by the Explosives Committee.

Abel, Sir James Dewar and Dr W Kellner, who was also on the committee, developed and jointly patented (Nos 5,614 and 11,664 in the names of Abel and Dewar) in 1889 a new ballistite-like propellant consisting of 58% nitroglycerine, by weight, 37% guncotton (nitrocellulose) and 5% petroleum jelly. Using acetone as a solvent, it was extruded as spaghetti-like rods initially called "cord powder" or "the Committee's modification of Ballistite", but this was swiftly abbreviated to "**Cordite**".

Cordite began as a *double-base* propellant. In the 1930s *triple-base* was developed by including a substantial proportion of nitroguanidine. Triple-based propellant reduced the disadvantages of double-base propellant - its relatively high temperature and significant flash, by combining two high explosives: nitrocellulose and nitroglycerine. ICI's World War 2 double-base **AN** formulation also had a much lower temperature, but it lacked the flash reduction properties of N and NQ triple-base propellants.

Whilst cordite is classified as an explosive, it is not employed as a high explosive. It is designed to deflagrate, or burn, to produce high pressure gases.

Cordite formulations

It was quickly discovered that the rate of burning could be varied by altering the surface area of the cordite. Narrow rods were used in small-arms and were relatively fast burning, while thicker rods would burn more slowly and were used for longer barrels, such as those used in artillery and naval guns.

Cordite (Mk I) and Cordite MD

The original Abel-Dewar formulation was soon superseded, as it caused excessive gun barrel erosion. It has since become known as **Cordite Mk I**.

The composition of cordite was changed to 65% guncotton and 30% nitroglycerine (keeping 5% petroleum jelly) shortly after the end of the Second Boer War. This was known as **Cordite MD** (modified).

Cordite MD cartridges typically weighed approximately 15% more than the cordite Mk I cartridges they replaced, to achieve the same muzzle velocity, due to the inherently less powerful nature of Cordite MD.[7]

Cordite RDB

During World War I acetone was in short supply in Great Britain, and a new experimental form was developed for use by the Royal Navy.[8] This was **Cordite RDB** (= **R**esearch **D**epartment formula **B**); which was 52% collodion, 42% nitroglycerine and 6% petroleum jelly. It was produced at HM Factory, Gretna;[8] and the Royal Navy Cordite Factory, Holton Heath.

Acetone for the cordite industry during late World War I was eventually produced through the efforts of Dr. Chaim Weizmann, considered to be the father of industrial fermentation. While a lecturer at Manchester University Weizmann discovered how to use bacterial fermentation to produce large quantities of many desired substances. He used the bacterium Clostridium acetobutylicum (the so-called Weizmann organism) to produce acetone. Weizmann transferred the rights to the manufacture of acetone to the Commercial Solvents Corporation in exchange for royalties. After the Shell Crisis of 1915 during World War I, he was director of the British Admiralty Laboratories from 1916 until 1919.

Cordite RDB was later found to become unstable if stored too long.

Cordite SC

Research on solvent-free Cordite RDB continued primarily on the addition of stabilizers, which led to the type commonly used in World War II as the main naval propellant. In Great Britain this was known as **Cordite SC** (= Solventless Cordite). Cordite SC was produced in different shapes and sizes, so the particular geometry of Cordite SC was indicated by the use of letters or numbers, or both, after the SC. For example, SC followed by a number was rod-shaped cord, with the number representing the diameter in thousandths of an inch. "SC T" followed by two sets of numbers indicated tubular propellant, with the numbers representing the two diameters in thousandths.

Two-inch (approximately 50 mm) and three-inch (approximately 75 mm) diameter, rocket Cordite SC charges were developed in great secrecy before World War II for anti-aircraft purposes—the so-called *Z batteries*, using Unrotated Projectiles.[1]

Cordite N

An important development during World War II was the addition of another explosive, nitroguanidine, to the mixture to form *triple-base* propellant or **Cordite N** and **NQ**. The formulations were slightly different for artillery and naval use. This solved two problems with the large naval guns of the day as fitted to capital ships. It was also used in limited amounts with 25-pr and 5.5-inch artillery. Nitroguanidine produces large amounts of nitrogen when heated, which had the benefit of reducing the muzzle flash, and its lower burning temperature greatly reduced the erosion of the gun barrel.

After World War II production of double based propellants generally ended. Triple based propellants, N and NQ, were the only ones used in new ammunition designs, such as the cartridges for 105mm Field and for 155mm FH70.

Cordite charge design

Cordite manufacture

UK Government factories

In Great Britain cordite was developed for military use at the Royal Arsenal, Woolwich, and at the Waltham Abbey Royal Gunpowder Mills from 1889 onwards.

In World War I a great cordite factory, HM Factory, Gretna, which straddled the Scotland-England border at Gretna was opened to manufacture cordite for the British Army and for British Commonwealth forces. A separate factory, The Royal Navy Cordite Factory, Holton Heath, was opened to manufacture cordite for the Royal Navy. Both the Gretna and the Holton Heath cordite factories closed at the end of World War I; and the Gretna factory was demolished.

By the start of World War II Holton Heath had reopened, and an additional factory for the Royal Navy, The Royal Navy Propellant Factory, Caerwent, opened at Caerwent in Wales. A very large Royal Ordnance Factory, ROF Bishopton, was opened in Scotland to manufacture cordite for the British Army and the Royal Air Force. A new cordite factory at Waltham Abbey and two additional ROF's—ROF Ranskill and ROF Wrexham—were also opened. Cordite produced in these factories was sent to Filling Factories for filling into ammunition.

MoS Agency Factories and ICI Nobel in World War II

The British Government set up additional cordite factories, not under Royal Ordnance Factory control but as Agency Factories run on behalf of the Ministry of Supply (MoS). The company of ICI Nobel, at Ardeer, was asked in 1939 to construct and operate six factories in southern Scotland. Four of these six were involved in cordite or firearm-propellant manufacture. The works at MoS Drungans (Dumfries) produced guncotton that was converted to cordite at MoS Dalbeattie (triple-base cordite) and at MoS Powfoot (monobase granulated guncotton for small-arms). A smaller site at Girvan, South Ayrshire, now occupied by Grant's distillery, produced cordite and TNT.[9] The ICI Ardeer site also had a mothballed World War I Government-owned cordite factory.[10]

35% of British cordite produced between 1942 and 1945 came from Ardeer and these agency factories.[11] ICI ran a similar works at Deer Park near Melbourne in Australia and in South Africa.[11]

Overseas supplies

Additional sources of propellant were also sought from the British Commonwealth in both World War I and World War II. Canada, South Africa and Australia, had ICI-owned factories that, in particular, supplied large quantities of cordite.

World War I

Canadian Explosives Limited was formed in 1910 to produce rifle cordite, at its Beloeil factory, for the Quebec Arsenal. By November 1915 production had been expanded to produce 350,000 lb (159,000 kg) of cordite per month for the Imperial Munitions Board.[12]

The Imperial Munitions Board set up a number of additional explosives factories in Canada. It built **The British Cordite Ltd** factory at Nobel, Ontario, in 1916/1917, to produce cordite. Production started in mid-1917.[12]

Canadian Explosives Limited built an additional cordite factory at Nobel, Ontario. Work stated in February 1918 and was finished on 24 August 1918. It was designed to produce 1,500,000 lb (681,000 kg) of cordite per month.[12]

Factories, specifically “heavy industry” (Long, and Marland 2009) ones, were very important to war and were a large source of the creation of munitions that soldiers needed during the war. Cordite factories were typically employed by women and this presented women’s involvement in the war effort (Cook 2006). The cordite factory workers put their life in danger every day they packed the shells but regardless of the risks they continued their work. Cordite factories and the dangerous work which was done inside improved and excelled the direction of war and the munitions soldiers had available to them.

In both the book and film of Frederick Forsyth's *The Day Of The Jackal* the assassin chews cordite to give his complexion a grey pallor so that he might impersonate an aged veteran.

References

Notes

1. ^ a b Brown 1999, Chapter 17
2. ^ Watters, Daniel, "The Great Propellant Controversy", *The Gun Zone*, retrieved 2009-11-30
3. ^ Hogg OFG, 'Artillery: Its Origin, Heyday and Decline', Hurst & Company, London, 1989
4. ^ http://www.aeragon.com/o/me/ni.html#ecpowder Aeragon Site Index > Ordnance > Military Explosives > Nitrocellulose > EC Powder
5. ^ a b Schuck & Sohlman 1929, pp. 136–144
6. ^ a b Schuck & Sohlman 1929, Appendix I: *Alfred Nobel's English lawsuit. Mr justice Romer's judgment in the "Cordite Case"*
7. ^ Example : BL 6-inch Mk VII gun : 20 lb cordite Mk I, 23 lb cordite MD. Table 8 in Treatise on Ammunition 1915.
8. ^ a b c d Ministry of Munitions of War
9. ^ Cocroft 2000, Gazetteer
10. ^ a b c d e Reader 1975, Chapter 14: "Warlike Supply"
11. ^ a b Reader 1975, Chapter 15: "War Production"
12. ^ a b c d Carnegie (1925).

Bibliography

- Bowditch, M.R.; Hayward, L. (1996). *A Pictorial record of the Royal Naval Cordite Factory: Holton Heath*. Wareham:: Finial Publishing. ISBN 1-900467-01-1.
- Brown, Donald (1999). *Somerset v Hitler: Secret Operations in the Mendips 1939 - 1945*. Newbury: Countryside Books. ISBN 1-85306-590-0.
- Carnegie, David (1925). *The History of Munitions Supply in Canada 1914-1918*. London: Longmans, Green and Co.
- Cocroft, Wayne D. (2000). *Dangerous Energy: The archaeology of gunpowder and military explosives manufacture*. Swindon: English Heritage. ISBN 1-85074-718-0.
- Davis, Tenney L. (1943). *The Chemistry of Powder and Explosives*. Volume II. New York: John Wiley & Sons.
- Hartcup, Guy (1970). *The Challenge of War: Scientific and Engineering Contributions to World War Two*. Newton Abbot:: David & Charles. ISBN 0-7153-4789-6.
- Reader, W.J. (1975). *Imperial Chemical Industries: A History. Volume II; The First Quarter-Century 1926-1952*. London: Oxford University Press. ISBN 0-19-215944-5.
- Schuck, H.; Sohlman, R. (1929). *The Life of Alfred Nobel*. London: William Heinemann.
- Ministry of Munitions of War (1919). *H.M. Factory, Gretna: Description of plant and process*. Dumfries: J. Maxwell and Son, for His Majesty's Stationery Office.
- Rotter, Andrew J. (2008). *Hiroshima: The World's Bomb*. Oxford: Oxford University Press. ISBN 0-19-280437-5.

- http://nigelef.tripod.com/ammo.htm#PROPELLANT

Collodion

Collodion is a flammable, syrupy solution of pyroxylin (a.k.a. "nitrocellulose", "cellulose nitrate", "flash paper", and "gun cotton") in ether and alcohol. There are two basic types; flexible and non-flexible. The flexible type is often used as a surgical dressing or to hold dressings in place. When painted on the skin, collodion dries to form a flexible nitrocellulose film. While it is initially colorless, it discolors over time. Non-flexible collodion is often used in theatrical make-up.

Anonymous "A Veteran with his Wife", ambrotype

Julia Margaret Cameron's "Alice Liddell as a Young Woman" print from wet collodion negative

In 1851, Frederick Scott Archer, an Englishman, discovered that collodion could be used as an alternative to egg white (albumen) on glass photographic plates. Collodion reduced the exposure time necessary for making an image. This method became known as the 'wet-plate collodion' or 'wet collodion' method. Collodion was relatively grainless and colorless, and allowed for one of the first high-quality duplication processes, also known as negatives. This process also produced positives, the ambrotype and the tintype (also known as ferrotype).

The process required great skill and included the following steps:

- Clean the glass plate (extremely well)
- In the light, pour "salted" (iodide, bromide) collodion onto the glass plate, tilting it so it reaches each corner. The excess is poured back into the bottle.
- Take the plate into a darkroom or orange tent (the plate is sensitive only to blue light) and immerse the plate in a silver nitrate sensitising bath (for 3–5 minutes)
- Lift the plate out of the bath, drain and wipe the back, load it into a plate holder and protect from light with a dark slide.
- Load the plate holder into the camera, withdraw the dark slide and expose the plate (can range from less than a second to several minutes)
- Develop the plate (using a ferrous sulfate based developer)
- Fix the plate (with potassium cyanide or sodium thiosulfate)

All of this was done in a matter of minutes, and some of the steps in (red) safelight conditions, which meant that the photographer had to carry the chemicals and a portable darkroom with him wherever he went. After these steps the plate needed rinsing in fresh water. Finally, the plate was dried and varnished using a varnish made from sandarac, alcohol and lavender oil.

Dark tents to be used outdoors consisted of a small tent that was tied around the photographer's waist. Otherwise a wheelbarrow or a horse and covered wagon were used.

Dry collodion plates

Richard Norris, a doctor of medicine and professor of physiology at Queen's College, Birmingham, is generally cred with the first development of dry collodion plate in the 1860s. In 1894 he took out a new patent for dry plate used in photography.

Medical

- Many wart-remover preparations consist of acetic acid and salicylic acid in an acetone collodion base used in the treatment of warts by keratolysis.
- Nitrocellulose (pyroxylin) solution is also used presently in 'MedTech's NewSkin' liquid bandage product.

[] Other uses

- Collodion is widely used to glue electrodes to the head for electro-encephalography.
- Non-flexible collodion is used in theatrical makeup for various effects. When applied to the skin, it shrinks as the solvent (usually ether or alcohol) evaporates, causing wrinkles and is used to simulate old age, or scars.
- Collodion is used in the cleaning of optics such as telescope mirrors. The collodion is applied to the surface of the optic, usually in two or more layers. Sometimes a piece of thin cloth is applied between the layers, to hold the collodion together for easy removal. After the collodion dries and forms a solid sheet covering the optic, it is carefully peeled away taking contamination with it.
- Collodion is a pure type of pyroxylin used to embed specimens which will be examined under a microscope.
- While in Paris René Dagron became familiar with the collodion wet plate and collodion-albumen dry plate processes which he would later adapt to his microfilm and Stanhope production techniques.
- Collodion was used by Alfred Nobel in his development of blasting gelatin, a more powerful, flexible, and water resistant variation on his highly successful product, Dynamite.
- Some types of nail polish also contain collodion.

Nitroglycerin

Nitroglycerin (**NG**), also known as **nitroglycerine**, **trinitroglycerin**, **trinitroglycerine**, or **nitro**, is more correctly known as **glyceryl trinitrate** or more formally: **1,2,3-trinitroxypropane**. It is a heavy, colorless, oily, explosive liquid most commonly produced by treating glycerol with white fuming nitric acid under conditions appropriate to the formation of the nitric acid ester. Chemically, the substance is an organic nitrate compound rather than a nitro compound, but the traditional name is often retained. Since the 1860s, nitroglycerin has been used as an active ingredient in the manufacture of explosives, mostly dynamite, and as such it is employed in the construction, demolition, and mining industries. Similarly, since the 1880s, it has been used by the military as an active ingredient, and a gelatinizer for nitrocellulose, in some solid propellants, such as Cordite and Ballistite.

Nitroglycerin is also a major component in double-based smokeless gunpowders used by reloaders. Combined with nitrocellulose, there are hundreds of (powder) combinations used by rifle, pistol, and shotgun reloaders.

Nitroglycerin is also used medically as a vasodilator to treat heart conditions, such as angina and chronic heart failure. Having been used for over 130 years, nitroglycerin is one of the oldest and most useful drugs for treating and preventing attacks of angina pectoris. Though it was previously known that these effects arise because nitroglycerin is converted to nitric oxide, a potent vasodilator, it was not until 2002 that the enzyme for this conversion was discovered to be mitochondrial aldehyde dehydrogenase.[2] Nitroglycerin comes in forms of tablets, sprays or patches.[3] It has been suggested for other uses also, such as an adjunct therapy in prostate cancer.[4]

[] History

Nitroglycerin was the first practical explosive ever produced that was stronger than black powder. Nitroglycerin was synthesized by the Italian chemist Ascanio Sobrero in 1847, working under Théophile-Jules Pelouze at the University of Turin. Sobrero initially called his discovery **pyroglycerine**, and warned vigorously against its use as an explosive. It was later adopted as a commercially useful explosive by Alfred Nobel. Nobel experimented with several safer ways to handle the dangerous nitroglycerin after his younger brother Emil Oskar Nobel and several factory workers were killed in a nitroglycerin explosion at the Nobel's armaments factory in 1864 in Heleneborg, Sweden.[5]

One year later, Alfred Nobel founded Alfred Nobel & Company in Germany and built an isolated factory in the Krümmel hills of Geesthacht near Hamburg. This business exported a liquid combination of nitroglycerin and gunpowder called "Blasting Oil", but this was extremely unstable and difficult to handle, as shown in numerous catastrophes. The buildings of the Krümmel factory were destroyed twice.[6]

In April 1866, three crates of nitroglycerin were shipped to California for the Central Pacific Railroad, which planned to experiment with it as a blasting explosive to expedite the construction of the 1,659-foot (506 m)-long Summit Tunnel through the Sierra Nevada Mountains. One of these crates exploded, destroying a Wells Fargo company office in San Francisco and killing 15 people. This led to a complete ban on the transportation of liquid nitroglycerin in California. The on-site manufacture of nitroglycerin was thus required for the remaining hard-rock drilling and blasting required for the completion of the First Transcontinental Railroad in North America.[7]

Liquid nitroglycerin was widely banned elsewhere as well, and these legal problems led to Alfred Nobel and his company's developing dynamite in 1867. This was made by mixing nitroglycerin with diatomaceous earth (called *"kieselgur"* in German) found in the Krümmel hills. Similar mixtures, such as "dualine" (1867), "lithofracteur" (1869), and "gelignite" (1875), were formed by mixing nitroglycerin with other inert absorbents, and many combinations were tried by other companies in attempts to get around Nobel's tightly held patents for dynamite.

Dynamite mixtures containing nitrocellulose, which increases the viscosity of the mix, are commonly known as "gelatins".

Following the discovery that amyl nitrite helped alleviate chest pain, Dr. William Murrell experimented with the use of nitroglycerin to alleviate angina pectoris and to reduce the blood pressure. He began treating his patients with small diluted doses of nitroglycerin in 1878, and this treatment was soon adopted into widespread use after Murrell published his results in the journal *The Lancet* in 1879.[8] A few months before his death in 1896, Alfred Nobel was prescribed nitroglycerine for this heart condition, writing to a friend: "Isn't it the irony of fate that I have been prescribed nitro-glycerin, to be taken internally! They call it Trinitrin, so as not to scare the chemist and the public."

[9] The medical establishment also used the name "glyceryl trinitrate" for the same reason.

[] Wartime production rates

Large quantities of nitroglycerin were manufactured during World War I and World War II for use as military propellants and in military engineering work. During World War I, HM Factory, Gretna, the largest propellant factory in the Great Britain, produced about 800 long tons (812 tonnes) of Cordite RDB per week. This amount took at least 336 tons of nitroglycerin per week (assuming no losses in production). The Royal Navy had its own factory at Royal Navy Cordite Factory, Holton Heath in Dorset, England. A large cordite factory was also built in Canada during World War I. The Canadian Explosives Limited cordite factory at Nobel, Ontario, was designed to produce 1,500,000 lb (680 t) of cordite per month. This required about 286 tonnes of nitroglycerin per month.

[] Instability and desensitization

In its pure form, nitroglycerin is a primary contact explosive, with physical shock causing it to explode, and it degrades over time to even more unstable forms. This makes nitroglycerin highly dangerous to transport or use. In this undiluted form, it is one of the world's most powerful explosives, comparable to the more recently-developed RDX and PETN, as well as the plastic explosive C-4—which contains 90 to 92 percent of RDX as its active ingredient.

Early in the history of nitroglycerin, it was discovered that liquid nitroglycerin can be "desensitized" by cooling it to about 5 to 10 °C (40 to 50 °F). At this temperature nitroglycerin freezes, contracting upon solidification. However, thawing it out can be extremely sensitizing, especially if impurities are present or if the warming is too rapid.[10] It is possible to chemically "desensitize" nitroglycerin to a point where it can be considered approximately as "safe" as modern high explosives, such as by the addition of approximately 10 to 30 percent ethanol, acetone,[11] or dinitrotoluene. (The percentage varies with the desensitizing agent used.) Desensitization requires extra effort to reconstitute the "pure" product. Failing this, it must be assumed that desensitized nitroglycerin is substantially more difficult to detonate, possibly rendering it useless as an explosive for practical application.

A serious problem in the use of nitroglycerin results from its high freezing point 13 °C (55 °F). Solid nitroglycerin is much less sensitive to shock than the liquid, a feature that is common in explosives. In the past, nitroglycerin was often shipped in the frozen state, but this resulted in a high number of accidents during the thawing process just before its use. This disadvantage is overcome by using mixtures of nitroglycerin with other polynitrates. For example, a mixture of nitroglycerin and ethylene glycol dinitrate freezes at −29 °C (−20 °F).[12]

[] Detonation

Nitroglycerin and any dilutents can certainly deflagrate, i.e. burn. However, the explosive power of nitroglycerin is derived from detonation: energy from the initial decomposition causes a pressure wave or gradient that detonates the surrounding fuel. This is a self-sustained shock wave that propagates through the explosive medium at some 30 times the speed of sound as a near-instantaneous pressure-induced decomposition of the fuel into a white hot gas. Detonation of nitroglycerin generates gases that would occupy more than 1,200 times the original volume at ordinary room temperature and pressure. Moreover, the heat liberated raises the temperature to about 5,000 °C (9,030 °F).[13] This is entirely different from deflagration, which depends solely upon available fuel regardless of pressure or shock. The decomposition results in much higher ratio of energy to gas moles released compared to other explosives, making it one of the hottest detonating high explosives.

[] Manufacturing

The industrial manufacturing process often uses a nearly 1:1 mixture of concentrated sulfuric acid and concentrated nitric acid. This can be produced by mixing white fuming nitric acid—a quite expensive pure nitric acid in which the oxides of nitrogen have been removed, as opposed to red fuming nitric acid, which contains nitrogen oxides—and concentrated sulfuric acid. More often, this mixture is attained by the cheaper method of mixing fuming sulfuric acid, also known as oleum—sulfuric acid containing excess sulfur trioxide—and azeotropic nitric acid (consisting of about 70 percent nitric acid, with the rest being water).

The sulfuric acid produces protonated nitric acid species, which are attacked by glycerin's nucleophilic oxygen atoms. The nitro group is thus added as an ester $C\text{-}O\text{-}NO_2$ and water is produced. This is different from an aromatic nitration reaction in which nitronium ions are the active species in an electrophilic attack on the molecule's ring system.

The addition of glycerin results in an exothermic reaction (i.e., heat is produced), as usual for mixed-acid nitrations. However, if the mixture becomes too hot, it results in "runaway", a state of accelerated nitration accompanied by the destructive oxidation of organic materials by the hot nitric acid and the release of poisonous nitrogen dioxide gas at high risk of an explosion. Thus, the glycerin mixture is added slowly to the reaction vessel containing the mixed acid (not acid to glycerin). The nitrator is cooled with cold water or some other coolant mixture and maintained throughout the glycerin addition at about 22 °C (72 °F), much below which the esterification occurs too slowly to be useful. The nitrator vessel, often constructed of iron or lead and generally stirred with compressed air, has an emergency trap door at its base, which hangs over a large pool of very cold water and into which the whole reaction mixture (called the charge) can be dumped to prevent an explosion, a process referred to as drowning. If the temperature of the charge exceeds about 30 °C (86 °F) (actual value varying by country) or brown fumes are seen in the nitrator's vent, then it is immediately drowned.

[] Use as an explosive and a propellant

Main articles: Dynamite, Ballistite, Cordite, smokeless powder, and Gelignite

Alfred Nobel's patent application from 1864.

The main use of nitroglycerin, by tonnage, is in explosives such as dynamite and in propellants.

Nitroglycerin is an oily liquid that may explode when subjected to heat, shock or flame. It is dangerously sensitive and dropping or bumping a container may cause it to explode.[14]

Alfred Nobel developed the use of nitroglycerin as a blasting explosive by mixing the nitroglycerin with inert absorbents, particularly *"kieselguhr,"* or diatomaceous earth. He named this explosive dynamite and patented it in 1867. It was supplied ready for use in the form of *sticks*, individually wrapped in greased water-proof paper. Dynamite and similar explosives were widely adopted for civil engineering tasks, such as in drilling highway and railroad tunnels, for mining, for clearing farmland of stumps, in quarrying, and in demolition work. Likewise, military engineers have used dynamite for construction and demolition work.

Nitroglycerin was also used as an ingredient in military propellants for use in firearms.

Nitroglycerin is a high explosive which is so sensitive that a slight jolt, friction, or impact may cause it to detonate. The molecule contains oxygen, nitrogen, and carbon with chemical bonds that are far less powerful than bonds that exist in a number of smaller molecules, particularly certain diatomic gases. Hence, when it explodes, great energy is released as the atoms rearrange to form new diatomic gas molecules with very strong bonds such as N_2, H_2O, and CO. It is the speed of the decomposition reaction which makes it such a violent explosive. A supersonic wave passing through the material causes it to decompose almost instantly. This instantaneous destruction of all molecules is called a detonation, and the destructive blast results from the rapid expansion of hot gases. Nitroglycerin has an advantage over some other high explosives, that practically no visible smoke is produced, therefore it acts as a "smokeless powder".[15]

Because of its extreme sensitivity, nitroglycerin was rendered obsolete as a military explosive, and was replaced by less sensitive explosives such as TNT, RDX, and HMX. Combat engineers still use dynamite.

Alfred Nobel then developed ballistite, by combining nitroglycerin and guncotton. He patented it in 1887. Ballistite was adopted by a number of European governments, as a military propellant. Italy was the first to adopt it. However, it was not adopted by the British Government. This government and the Commonwealth governments, adopted cordite, which had been developed by Sir Frederick Abel and Sir James Dewar of the United Kingdom in 1889. The original Cordite Mk I consisted of 58% nitroglycerin, 37% guncotton, and 5.0% petroleum jelly. Ballistite and cordite were both manufactured in the forms of *cords*.

Smokeless powders were originally developed using nitrocellulose as the sole explosive ingredient. Therefore they were known as *single base* propellants. A range of smokeless powders that contain both nitrocellulose and nitroglycerin, known as *double base* propellants, were also developed. Smokeless powders were originally supplied only for military use, but they were also soon developed for civilian use and were quickly adopted for sports. Some are known as sporting powders. *Triple base* propellants contain nitrocellulose, nitroglycerin, and nitroguanidine, but are reserved mainly for extremely high caliber ammunition rounds such as those used in tank cannons and naval artillery.

Blasting gelatin, also known as gelignite, was invented by Nobel in 1875, using nitroglycerin, wood pulp, and sodium or potassium nitrates. This was an early low-cost, flexible explosive.

[] Dynamite

Alfred Nobel discovered that mixing nitroglycerin with diatomaceous earth would turn the liquid into a paste, called dynamite. An advantage of dynamite was that it could be cylinder-shaped for insertion into the drilling holes used for mining and tunneling. Nobel received the American patent number 78,317 for his dynamite in 1867.[16]

[] Medical use

Main article: Glyceryl trinitrate (pharmacology)

Nitroglycerin was first used by William Murrell to treat anginal attacks in 1878, with the discovery published in 1878.[8][17]

Nitroglycerin belongs to a group of drugs called nitrates, which includes many other nitrates like isosorbide dinitrate (Isordil) and isosorbide mononitrate (Imdur, Ismo, Monoket).[18] These agents all exert their effect by being converted to nitric oxide in the body by mitochondrial aldehyde dehydrogenase,[2] and nitric oxide is a potent natural vasodilator.

In medicine, where it is generally called glyceryl trinitrate, nitroglycerin is used as a heart medication. It is used as a medicine for angina pectoris (ischemic heart disease) in tablets, ointment, solution for intravenous use, transdermal patches, or sprays administered sublingually. Patients who experience angina when doing certain physical activities can often prevent symptoms by taking nitroglycerin 5 to 10 minutes before the activity. Some forms of nitroglycerin last much longer in the body than others. These may come in the form of a pill taken one, two, or three times per day, or even as a patch. It has been shown that round-the-clock exposure to nitrates can cause the body to stop responding normally to this medicine. Experts recommend that the patches be removed at night, allowing the body a few hours to restore its responsiveness to nitrates. Shorter-acting preparations can be used several times a day with less risk of the body getting used to this drug.[19]

Angina pectoris is due to an inadequate flow of blood and oxygen to the heart. It is believed that nitroglycerin corrects the imbalance between the flow of oxygen and blood to the heart.[20] The principal action of nitroglycerin is vasodilation—widening of the blood vessels. At low doses, nitroglycerin will dilate veins more than arteries, but at higher doses it also dilates arteries and is a potent antihypertensive agent. In cardiac treatment the lowering of pressure in the arteries reduces the pressure against which the heart must pump, thereby decreasing afterload.[18] Dilating the veins decreases cardiac preload and leads to the following therapeutic effects during episodes of angina pectoris: subsiding of chest pain, decrease of blood pressure, increase of heart rate, and orthostatic hypotension.

Industrial exposure

Infrequent exposure to high doses of nitroglycerin can cause severe headaches known as "NG head" or "bang head". These headaches can be severe enough to incapacitate some people; however, humans develop a tolerance to and dependence on nitroglycerin after long-term exposure. Withdrawal can (rarely) be fatal;[21] withdrawal symptoms include headaches and heart problems and if unacceptable may be treated with re-exposure to nitroglycerin or other suitable organic nitrates.[22]

For workers in nitroglycerin (NTG) manufacturing facilities, the effects of withdrawal sometimes include a "Monday morning headache" in those who experience regular nitroglycerin exposure in the workplace leading to the development of tolerance for the vasodilating effects. Over the weekend the workers lose the tolerance and when they are re-exposed on Monday the drastic vasodilation produces tachycardia, dizziness, and a headache.[23]

References

1. ^ a b http://www.osha.gov/SLTC/healthguidelines/nitroglycerin/recognition.html
2. ^ a b Chen et al.; Foster, MW; Zhang, J; Mao, L; Rockman, HA; Kawamoto, T; Kitagawa, K; Nakayama, KI et al. (2005). "An essential role for mitochondrial aldehyde dehydrogenase in nitroglycerin bioactivation". *Proc. Natl. Acad. Sci. USA* **102** (34): 12159–12164. doi:10.1073/pnas.0503723102. PMC 1189320. PMID 16103363.
3. ^ Feb97, Vol. 7, Issue 6
4. ^ Daily Mail: "How dynamite could help destroy prostate cancer" Retrieved 2010-02-23
5. ^ NobelPrize.org: Emil Nobel.
6. ^ NobelPrize.org: Krümmel.
7. ^ "Transcontinental Railroad – People & Events: Nitroglycerin", *American Experience*, PBS.
8. ^ a b Sneader, Walter. *Drug Discovery: A History*. John Wiley and Sons, 2005 ISBN 0-471-89980-1.
9. ^ History of TNG
10. ^ "Tales of Destruction-Thawing can be Hell".
11. ^ "Tales of Destruction – Is Nitroglicerine in This?".
12. ^ "nitroglycerin". *Britannica*. Retrieved 2005-03-23.
13. ^ Encyclopaedia Britannica.
14. ^ Ch. 3: Explosives and Bombs 1998
15. ^ An explosive combination of atoms
16. ^ About.com
17. ^ William Murrell biography
18. ^ a b Nitroglycerin Article
19. ^ Nitroglycerin for angina, February 1997, Vol. 7.
20. ^ http://www.medicinenet.com/nitroglycerin/article.htm
21. ^ Amdur, Mary O.; Doull, John. Casarett and Doull's Toxicology. 4th ion Pub: Elsevier 1991 ISBN: 0071052399
22. ^ John B. Sullivan, Jr.; Gary R. Krieger (2001). *Clinical Environmental Health and Toxic Exposures: Latex*. Lippincott Williams & Wilkins. pp. 264–. ISBN 978-0-683-08027-8. Retrieved 23 April 2013.
23. ^ Assembly of Life Sciences (U.S.). Advisory Center on Toxicology. *Toxicological Reports*. National Academies. pp. 115–. NAP:11288. Retrieved 23 April 2013.

[] External links

- "Nitroglycerine! Terrible Explosion and Loss of Lives in San Francisco". *Central Pacific Railroad Photographic History Museum*. Retrieved 2005-03-23.– 1866 Newspaper article
- WebBook page for C3H5N3O9
- The Tallini Tales of Destruction Detailed and horrific stories of the historical use of nitroglycerin-filled torpedoes to restart petroleum wells.
- Dynamite and TNT at *The Periodic Table of Videos* (University of Nottingham)

Smokeless powder

Finnish smokeless powder

Smokeless powder is the name given to a number of propellants used in firearms and artillery which produce negligible smoke when fired, unlike the older gunpowder (black powder) which they replaced. It is a term peculiar to the United States and is not generally used in other English speaking countries, who initially adopted the term "Cordite" but gradually changed to "propellant".

The basis of the term smokeless is that the combustion products are mainly gaseous, compared to around 55% solid products (mostly potassium carbonate, potassium sulfate, and potassium sulfide) for black powder.[1] Despite its name, smokeless powder is not completely smoke-free;[2] while there may be little noticeable smoke from small-arms ammunition, smoke from artillery fire can be substantial. This article focuses on nitrocellulose formulations, but the term smokeless powder was also used to describe various picrate mixtures with nitrate, chlorate, or dichromate oxidizers during the late 19th century, before the advantages of nitrocellulose became evident.[3]

Since the 14th century[4] gunpowder was not actually a physical "powder," and smokeless powder can only be produced as a pelletized or extruded granular material. Smokeless powder allowed the development of modern semi- and fully automatic firearms and lighter breeches and barrels for artillery. Burnt black powder leaves a thick, heavy fouling which is hygroscopic and causes rusting of the barrel. The fouling left by smokeless powder exhibits none of these properties. This makes an autoloading firearm with many moving parts feasible (which would otherwise jam or seize under heavy black powder fouling).

Smokeless powders are classified as, typically, division 1.3 explosives under the UN *Recommendations on the transportation of Dangerous goods – Model Regulations*, regional regulations (such as ADR) and national regulations (such the United States' ATF). However, they are used as solid propellants; in normal use, they undergo deflagration rather than detonation.

[] Background

Military commanders had been complaining since the Napoleonic Wars about the problems of giving orders on a battlefield obscured by the smoke of firing. Verbal commands could not be heard above the noise of the guns, and visual signals could not be seen through the thick smoke from the gunpowder used by the guns. Unless there was a strong wind, after a few shots, soldiers using black powder ammunition would have their view obscured by a huge cloud of smoke. Snipers or other concealed shooters were given away by a cloud of smoke over the firing position. Black powder is also corrosive, making cleaning mandatory after every use. Likewise, black powder's tendency to produce severe fouling caused actions to jam and often made reloading difficult.

[] Nitroglycerine and guncotton

Nitroglycerine was discovered by Professor Sobrero in Turin in 1846. It was subsequently developed and manufactured by Alfred Nobel as an explosive substance, but it was unsuitable as a propellant. A major step forward was the discovery of guncotton, a nitrocellulose-based material, by Swiss chemist Christian Friedrich Schönbein in 1846. He promoted its use as a blasting explosive[5] and sold manufacturing rights to the Austrian Empire. Guncotton was more powerful than gunpowder, but at the same time was somewhat more unstable. John Taylor obtained an English patent for guncotton; and John Hall & Sons began manufacture in Faversham. English interest languished after an explosion destroyed the Faversham factory in 1847. Austrian Baron von Lenk built two guncotton plants producing artillery propellent, but it was dangerous under field conditions, and guns that could fire thousands of rounds using gunpowder would reach their service life after only a few hundred shots with the more powerful guncotton. Small arms could not withstand the pressures generated by guncotton. After one of the Austrian factories blew up in 1862, Thomas Prentice & Company began manufacturing guncotton in Stowmarket in 1863; and British War Office chemist Sir Frederick Abel began thorough research at Waltham Abbey Royal Gunpowder Mills leading to a manufacturing process that eliminated the impurities in nitrocellulose making it safer to produce and a stable product safer to handle. Abel patented this process in 1865, when the second Austrian guncotton factory exploded. After the Stowmarket factory exploded in 1871, Waltham Abbey began production of guncotton for torpedo and mine warheads.[6]

[] Propellant improvements

In 1863, Prussian artillery captain Johann F. E. Schultze patented a small arms propellent of nitrated hardwood impregnated with saltpetre or barium nitrate. Prentice received an 1866 patent for a sporting powder of nitrated paper manufactured at Stowmarket, but ballistic uniformity suffered as the paper absorbed atmospheric moisture. In 1871, Frederick Volkmann received an Austrian patent for a colloided version of Schultze powder called *Collodin* which he manufactured near Vienna for use in sporting firearms. Austrian patents were not published at the time, and the Austrian Empire considered the operation a violation of the government monopoly on explosives manufacture and closed the Volkmann factory in 1875.[6] In 1882, the Explosives

Company at Stowmarket patented an improved formulation of nitrated cotton gelatinised by ether-alcohol with nitrates of potassium and barium. These propellants were suitable for shotguns but not rifles.[7]

Poudre B single-base smokeless powder flakes

In 1884, Paul Vieille invented a smokeless powder called Poudre B (short for *poudre blanche* -- white powder, as distinguished from black powder)[8] made from 68.2% insoluble nitrocellulose, 29.8% soluble nitrocellusose gelatinized with ether and 2% paraffin. This was adopted for the Lebel rifle.[9] It was passed through rollers to form paper thin sheets, which were cut into flakes of the desired size.[8] The resulting propellant, today known as *pyrocellulose*, contains somewhat less nitrogen than guncotton and is less volatile. A particularly good feature of the propellant is that it will not detonate unless it is compressed, making it very safe to handle under normal conditions.

Vieille's powder revolutionized the effectiveness of small guns, because it gave off almost no smoke and was three times more powerful than black powder. Higher muzzle velocity meant a flatter trajectory and less wind drift and bullet drop, making 1000 meter shots practicable. Since less powder was needed to propel a bullet, the cartridge could be made smaller and lighter. This allowed troops to carry more ammunition for the same weight. Also, it would burn even when wet. Black powder ammunition had to be kept dry and was almost always stored and transported in watertight cartridges.

Other European countries swiftly followed and started using their own versions of Poudre B, the first being Germany and Austria which introduced new weapons in 1888. Subsequently Poudre B was modified several times with various compounds being added and removed. Krupp began adding diphenylamine as a stabilizer in 1888.[6]

Meanwhile, in 1887, Alfred Nobel obtained an English patent for a smokeless gunpowder he called Ballistite. In this propellant the fibrous structure of cotton (nitro-cellulose) was destroyed by a nitro-glycerine solution instead of a solvent.[10] In England in 1889, a similar powder was patented by Hiram Maxim, and in the USA in 1890 by Hudson Maxim.[11] Ballistite was patented in the United States in 1891.

The Germans adopted ballistite for naval use in 1898, calling it WPC/98. The Italians adopted it as *filite*, in cord instead of flake form, but realising its drawbacks changed to a formulation with nitroglycerine they called *solenite*. In 1891 the Russians tasked the chemist Mendeleef with finding a suitable propellant, he created nitrocellulose gelatinised by ether-alcohol, which produced more nitrogen and more uniform colloidal structure than the French use of nitro-cottons in Poudre B. He called it pyro-collodion.[10]

Britain conducted trials on all the various types of propellant brought to their attention, but were dissatified with them all and sought something superior to all existing types. In 1889, Sir Frederick Abel, James Dewar and Dr W Kellner patented (Nos 5614 and 11,664 in the names of Abel and Dewar) a new formulation that was manufactured at the Royal Gunpowder Factory at Waltham Abbey. It entered British service in 1891 as Cordite Mark 1. Its main composition was 58% Nitro-glycerine, 37% Guncotton and 3% mineral jelly. A modified version, Cordite MD, entered service in 1901, this increased guncotton to 65% and reduced nitro-glycerine to 30%, this change reduced the combustion temperature and hence erosion and barrel wear. Cordite's advantages over gunpowder were reduced maximum pressure in the chamber (hence lighter breeches, etc.) but longer high pressure. Cordite could be made in any desired shape or size.[12] The creation of cordite led to a lengthy court battle between Nobel, Maxim, and another inventor over alleged British patent infringement.

The Anglo-American Explosives Company began manufacturing its shotgun powder in Oakland, New Jersey in 1890. DuPont began producing guncotton at Carneys Point Township, New Jersey in 1891.[3] Charles E. Munroe of the Naval Torpedo Station in Newport, Rhode Island patented a formulation of guncotton colloided with nitrobenzene, called *Indurite*, in 1891.[13] Several United States firms began producing smokeless powder when Winchester Repeating Arms Company started loading sporting cartridges with Explosives Company powder in 1893. California Powder Works began producing a mixture of nitroglycerine and nitrocellulose with ammonium picrate as *Peyton Powder*, Leonard Smokeless Powder Company began producing nitroglycerine-nitrocellulose *Ruby* powders, Laflin & Rand negotiated a license to produce *Ballistite*, and DuPont started producing smokeless shotgun powder. The United States Army evaluated 25 varieties of smokeless powder and selected *Ruby* and *Peyton Powders* as the most suitable for use in the Krag-Jørgensen service rifle. *Ruby* was preferred, because tin-plating was required to protect brass cartridge cases from picric acid in the *Peyton Powder*. Rather than paying the required royalties for *Ballistite*, Laflin & Rand financed Leonard's reorganization as the American Smokeless Powder Company. United States Army Lieutenant Whistler assisted American Smokeless Powder Company factory superintendent Aspinwall in formulating an improved powder named W.A. for their efforts. W.A. smokeless powder was the standard for United States military service rifles from 1897 until 1908.[3]

In 1897, United States Navy Lieutenant John Bernadou patented a nitrocellulose powder colloided with ether-alcohol.[13] The Navy licensed or sold patents for this formulation to DuPont and the California Powder Works while retaining manufacturing rights for the Naval Powder Factory, Indian Head, Maryland constructed in 1900. The United States Army adopted the Navy single-base formulation in 1908 and began manufacture at Picatinny Arsenal.[3] By that time Laflin & Rand had taken over the American Powder Company to protect their investment, and Laflin & Rand had been purchased by DuPont in 1902.[14] Upon securing a 99-year lease of the Explosives Company in 1903, DuPont enjoyed use of all significant smokeless powder patents in the United States, and was able to optimize production of smokeless powder.[3] When government anti-trust action forced divestiture in 1912, DuPont retained the nitrocellulose smokeless powder formulations used by the United States military and released the double-base formulations used in sporting ammunition to the reorganized Hercules Powder Company. These newer propellants were more stable and thus safer to handle than Poudre B, and also more powerful.

[] Chemical formulations

"Double base" redirects here. For the musical instrument, see double bass.

Currently, propellants using nitrocellulose (detonation velocity 7,300 m/s) (typically an ether-alcohol colloid of nitrocellulose) as the sole explosive propellant ingredient are described as **single-base powder**.[15]

Propellants mixtures containing nitrocellulose and nitroglycerin (detonation velocity 7,700 m/s) as explosive propellant ingredients are known as **double-base powder**.[16]

During the 1930s **triple-base propellant** containing nitrocellulose, nitroglycerin, and a substantial quantity of nitroguanidine (detonation velocity 8,200 m/s) as explosive propellant ingredients was developed. These propellant mixtures have reduced flash and flame temperature without sacrificing chamber pressure compared to single and double base propellants, albeit at the cost of more smoke.
In practice, triple base propellants are reserved mainly for large caliber ammunition such as used in (naval) artillery and tank guns. During World War II it had some use by British artillery. After that war it became the standard propellant in all British large caliber ammunition designs except small-arms. Most western nations, except the United States, followed a similar path.

In the late 20th century new propellant formulations started to appear. These are based on nitroguanidine and high explosives of the RDX (detonation velocity 8,750 m/s) type.

[] Instability and stabilization

Nitrocellulose deteriorates with time, yielding acidic byproducts. Those byproducts catalyze the further deterioration, increasing its rate. The released heat, in case of bulk storage of the powder, or too large blocks of solid propellant, can cause self-ignition of the material. Single-base nitrocellulose propellants are hygroscopic and most susceptible to degradation; double-base and triple-base propellants tend to deteriorate more slowly. To neutralize the decomposition products, which could otherwise cause corrosion of metals of the cartridges and gun barrels, calcium carbonate is added to some formulations.

To prevent buildup of the deterioration products, stabilizers are added. Diphenylamine is one of the most common stabilizers used. Nitrated analogs of diphenylamine formed in the process of stabilizing decomposing powder are sometimes used as stabilizers themselves.[17][18] The stabilizers are added in the amount of 0.5–2% of the total amount of the formulation; higher amounts tend to degrade its ballistic properties. The amount of the stabilizer is depleted with time. Propellants in storage should be periodically tested for the amount of stabilizer remaining, as its depletion may lead to auto-ignition of the propellant.

[] Physical variations

Ammunition handloading powders

Smokeless powder may be corned into small spherical balls or extruded into cylinders or strips with many cross-sectional shapes (strips with various rectangular proportions, single or multi-hole cylinders, slotted cylinders) using solvents such as ether. These extrusions can be cut into short ('flakes') or long pieces ('cords' many inches long). Cannon powder has the largest pieces.

The properties of the propellant are greatly influenced by the size and shape of its pieces. The specific surface area of the propellant influences the speed of burning, and the size and shape of the particles determine the specific surface area. By manipulation of the shape it is possible to influence the burning rate and hence the rate at which pressure builds during combustion. Smokeless powder burns only on the surfaces of the pieces. Larger pieces burn more slowly, and the burn rate is further controlled by flame-deterrent coatings which retard burning slightly. The intent is to regulate the burn rate so that a more or less constant pressure is exerted on the propelled projectile as long as it is in the barrel so as to obtain the highest velocity. The perforations stabilize the burn rate because as the outside burns inward (thus shrinking the burning surface area) the inside is burning outward (thus increasing the burning surface area, but faster, so as to fill up the increasing volume of barrel presented by the departing projectile).[19] Fast-burning pistol powders are made by extruding shapes with more area such as flakes or by flattening the spherical granules. Drying is usually performed under a vacuum. The solvents are condensed and recycled. The granules are also coated with graphite to prevent static electricity sparks from causing undesired ignitions.[20]

Faster-burning propellants generate higher temperatures and higher pressures, however they also increase wear on gun barrels.

[] Smokeless propellant components

The propellant formulations may contain various energetic and auxiliary components:

- Propellants:
    - Nitrocellulose, an energetic component of most smokeless propellants[21]
    - Nitroglycerin, an energetic component of double-base and triple-base formulations[21]
    - Nitroguanidine, a component of triple-base formulations[21]
    - D1NA (bis-nitroxyethylnitramine)[22]
    - Fivonite (tetramethylolcyclopentanone)[22]
    - DGN (di-ethylene glycol dinitrate)[23]
    - Acetyl cellulose[24]
- Deterrents, (or moderants), to slow the burning rate
    - Centralites (symmetrical diphenyl urea—primarily diethyl or dimethyl)[25][26]
    - Dibutyl phthalate[21][26]
    - Dinitrotoluene (toxic, carcinogenic, and obsolete)[21][27]
    - Akardite (asymmetrical diphenyl urea)[23]
    - ortho-tolyl urethane[28]
    - Polyester adipate
    - Camphor (obsolete)[26]
- Stabilizers, to prevent or slow down self-decomposition[29]
    - Diphenylamine[30]
    - Petroleum jelly[31]
    - Calcium carbonate[21]
    - Magnesium oxide[23]
    - Sodium bicarbonate[24]
    - beta-naphthol methyl ether[28]
    - Amyl alcohol (obsolete)[32]
    - Aniline (obsolete)[33]
- Decoppering additives, to hinder the buildup of copper residues from the gun barrel rifling
    - Tin metal and compounds (e.g., tin dioxide)[21][34]
    - Bismuth metal and compounds (e.g., bismuth trioxide, bismuth subcarbonate, bismuth nitrate, bismuth antimonide); the bismuth compounds are favored as copper dissolves in molten bismuth, forming brittle and easily removable alloy
    - Lead foil and lead compounds, phased out due to toxicity[22]
- Flash reducers, to reduce the brightness of the muzzle flash (all have a disadvantage: the production of smoke)[35]

    - Potassium chloride[36]
    - Potassium nitrate
    - Potassium sulfate[21][34]
    - Potassium hydrogen tartarate (a byproduct of wine production formerly used by French artillery)[36]
- Wear reduction additives, to lower the wear of the gun barrel liners[37]
    - Wax
    - Talc
    - Titanium dioxide
    - Polyurethane jackets over the powder bags, in large guns
- Other additives
    - Ethyl acetate, a solvent for manufacture of spherical powder[31]
    - Rosin, a surfactant to hold the grain shape of spherical powder
    - Graphite, a lubricant to cover the grains and prevent them from sticking together, and to dissipate static electricity[20]

[] Manufacturing

This section describes procedures used in the United States. See Cordite for alternative procedures formerly used in the United Kingdom.

The United States Navy manufactured single-base tubular powder for naval artillery at Indian Head, Maryland, beginning in 1900. Similar procedures were used for United States Army production at Picatinny Arsenal beginning in 1907[15] and for manufacture of smaller grained Improved Military Rifle (IMR) powders after 1914. Short-fiber cotton linter was boiled in a solution of sodium hydroxide to remove vegetable waxes, and then dried before conversion to nitrocellulose by mixing with concentrated nitric and sulfuric acids. Nitrocellulose still resembles fibrous cotton at this point in the manufacturing process, and was typically identified as pyrocellulose because it would spontaneously ignite in air until unreacted acid was removed. The term guncotton was also used; although some references identify guncotton as a more extensively nitrated and refined product used in torpedo and mine warheads prior to use of TNT.[38]

Unreacted acid was removed from pyrocellulose pulp by a multistage draining and water washing process similar to that used in paper mills during production of chemical woodpulp. Pressurized alcohol removed remaining water from drained pyrocellulose prior to mixing with ether and diphenylamine. The mixture was then fed through a press extruding a long turbular cord form to be cut into grains of the desired length.[39]

Alcohol and ether were then evaporated from "green" powder grains to a remaining solvent concentration between 3 percent for rifle powders and 7 percent for large artillery powder grains. Burning rate is inversely proportional to solvent concentration. Grains were coated with electrically conductive graphite to minimize generation of static electricity during subsequent blending. "Lots" containing more than ten tonnes of powder grains were mixed through a tower arrangement of blending hoppers to minimize ballistic differences. Each blended lot was then subjected to testing to determine the correct loading charge for the desired performance.[40][41]

Military quantities of old smokeless powder were sometimes reworked into new lots of propellants.[42] Through the 1920s Dr. Fred Olsen worked at Picatinny Arsenal experimenting with ways to salvage tons of single-base cannon powder manufactured for World War I. Dr. Olsen was employed by Western Cartridge Company in 1929 and developed a process for manufacturing spherical smokeless powder by 1933.[43] Reworked powder or washed pyrocellulose can be dissolved in ethyl acetate containing small quantities of desired stabilizers and other additives. The resultant syrup, combined with water and surfactants, can be heated and agitated in a pressurized container until the syrup forms an emulsion of small spherical globules of the desired size. Ethyl acetate distills off as pressure is slowly reduced to leave small spheres of nitrocellulose and additives. The spheres can be subsequently modified by adding nitroglycerine to increase energy, flattening between rollers to a uniform minimum dimension, coating with phthalate deterrents to retard ignition, and/or glazing with graphite to improve flow characteristics during blending.[44][45]

[] Flashless propellant

Muzzle flash is the light emitted in the vicinity of the muzzle by the hot propellant gases and the chemical reactions that follow as the gases mix with the surrounding air. Before projectiles exit a slight pre-flash may occur from gases leaking past the projectiles. Following muzzle exit the heat of gases is usually sufficient to emit visible radiation – the primary flash. The gases expand but as they pass through the Mach disc they are re-compressed to produce an intermediate flash. Hot combustible gases (e.g. hydrogen and carbon-monoxide) may follow when they mix with oxygen in the surrounding air to produce the secondary flash, the brightest. The secondary flash does not usually occur with small-arms.[46]

Nitrocellulose contains insufficient oxygen to completely oxidize its carbon and hydrogen. The oxygen deficit is increased by addition of graphite and organic stabilizers. Products of combustion within the gun barrel include flammable gasses like hydrogen and carbon monoxide. At high temperature, these flammable gasses will ignite when turbulently mixed with atmospheric oxygen beyond the muzzle of the gun. During night engagements the flash produced by ignition can reveal the location of the gun to enemy forces[47] and cause temporary night-blindness among the gun crew by photo-bleaching visual purple.[48]

Flash suppressors are commonly used on small arms to reduce the flash signature, but this approach is not practical for artillery. Artillery muzzle flash up to 150 feet (46 m) from the muzzle has been observed, and can be reflected off clouds and be visible for distances up to 30 miles (48 km).[47] For artillery the most effective method is a propellant that produces a large proportion of inert nitrogen at relatively low temperatures that dilutes the combustible gases. Triple based propellants are used for this because of the nitrogen in the nitroguandine.[49]

Before the use of triple based propellants the usual method of flash reduction was to add inorganic salts like potassium chloride so their specific heat capacity might reduce the temperature of combustion gasses and their finely divided particulate smoke might block visible wavelengths of radiant energy of combustion.[36]

[] See also

Pyrotechnics portal

- Antique guns
- Ballistite
- Cordite
- Firearms
- Gunpowder
- Nitrocellulose
- Small arms
- Brown-brown – a drug created by mixing cocaine with cartridge powder

[] References

[] Notes

1. ^ Hatcher, Julian S. and Barr, Al *Handloading* Hennage Lithograph Company (1951) p.34
2. ^ Fairfield, A. P., CDR USN *Naval Ordnance* Lord Baltimore Press (1921) p.44
3. ^ *a b c d e* Sharpe, Philip B. *Complete Guide to Handloading* 3rd Edition (1953) Funk & Wagnalls pp.146-149
4. ^ seegunpowder
5. ^ Davis, William C., Jr. *Handloading* National Rifle Association of America (1981) p.28
6. ^ *a b c* Sharpe, Philip B. *Complete Guide to Handloading* 3rd Edition (1953) Funk & Wagnalls pp.141-144
7. ^ Hogg, Oliver F. G. *Artillery: Its Origin, Heyday and Decline* (1969) p.138-139
8. ^ *a b* Davis, Tenney L. *The Chemistry of Powder & Explosives* (1943) pages 289–292
9. ^ Hogg, Oliver F. G. *Artillery: Its Origin, Heyday and Decline* (1969) p.139
10. ^ *a b* Hogg, Oliver F. G. *Artillery: Its Origin, Heyday and Decline* (1969) p.140
11. ^ **U.S. Patent 430,212** – *Manufacture of explosive* – H. S. Maxim
12. ^ Hogg, Oliver F. G. *Artillery: Its Origin, Heyday and Decline* (1969) p.141
13. ^ *a b* Davis, Tenney L. *The Chemistry of Powder & Explosives* (1943) pages 296-297
14. ^ "Laflin & Rand Powder Company". DuPont. Retrieved 2012-02-24.
15. ^ *a b* Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) p.297
16. ^ Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) p.298
17. ^ Fairfield, A. P., CDR USN *Naval Ordnance* Lord Baltimore Press (1921) p.28
18. ^ Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) p. 310
19. ^ Fairfield, A. P., CDR USN *Naval Ordnance* Lord Baltimore Press (1921) pp.41–43
20. ^ *a b* Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) p.306
21. ^ *a b c d e f g h* Campbell, John *Naval Weapons of World War Two* (1985) p. 5
22. ^ *a b c* Campbell, John *Naval Weapons of World War Two* (1985) p. 104
23. ^ *a b c* Campbell, John *Naval Weapons of World War Two* (1985) p. 221
24. ^ *a b* Campbell, John *Naval Weapons of World War Two* (1985) p. 318
25. ^ Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) pages 317–320
26. ^ *a b c* Davis, William C., Jr. *Handloading* National Rifle Association of America (1981) p.30
27. ^ Davis, William C., Jr. *Handloading* National Rifle Association of America (1981) p.31
28. ^ *a b* Campbell, John *Naval Weapons of World War Two* (1985) p. 174

29. ^ Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) pages 307–311
30. ^ Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) p. 302
31. ^ *a* *b* Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) p. 296
32. ^ Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) p. 307
33. ^ Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) p. 308
34. ^ *a* *b* Davis, William C., Jr. *Handloading* National Rifle Association of America (1981) p.32
35. ^ Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) pages 322–327
36. ^ *a* *b* *c* Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) pages 323–327
37. ^ "USA 16"/50 (40.6 cm) Mark 7". NavWeaps. 2008-11-03. Retrieved 2008-12-05.
38. ^ Fairfield, A. P., CDR USN *Naval Ordnance* Lord Baltimore Press (1921) pages 28–31
39. ^ Fairfield, A. P., CDR USN *Naval Ordnance* Lord Baltimore Press (1921) pages 31–35
40. ^ Fairfield, A. P., CDR USN *Naval Ordnance* Lord Baltimore Press (1921) pages 35–41
41. ^ Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) pages 293 & 306
42. ^ Fairfield, A. P., CDR USN *Naval Ordnance* Lord Baltimore Press (1921) p.39
43. ^ Matunas, E. A. *Winchester-Western Ball Powder Loading Data* Olin Corporation (1978) p.3
44. ^ Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) pages 328–330
45. ^ Wolfe, Dave *Propellant Profiles Volume 1* Wolfe Publishing Company (1982) pages 136–137
46. ^ Moss G. M., Leeming D. W., Farrar C. L. *Military Ballisitcs* (1969) pages 55–56
47. ^ *a* *b* Davis, Tenny L. *The Chemistry of Powder & Explosives* (1943) pages 322–323
48. ^ Milner p.68
49. ^ Moss G. M., Leeming D. W., Farrar C. L. *Military Ballisitcs* (1969) pages 59–60

[] Sources

- Campbell, John (1985). *Naval Weapons of World War Two*. Naval Institute Press. ISBN 0-87021-459-4.
- Davis, Tenney L. (1943). *The Chemistry of Powder & Explosives* (Angriff Press [1992] ed.). John Wiley & Sons Inc. ISBN 0-913022-00-4.
- Davis, William C., Jr. (1981). *Handloading*. National Rifle Association of America. ISBN 0-935998-34-9.
- Fairfield, A. P., CDR USN (1921). *Naval Ordnance*. Lord Baltimore Press.
- Hatcher, Julian S. and Barr, Al (1951). *Handloading*. Hennage Lithograph Company.
- Matunas, E. A. (1978). *Winchester-Western Ball Powder Loading Data*. Olin Corporation.
- Milner, Marc (1985). *North Atlantic Run*. Naval Institute Press. ISBN 0-87021-450-0.
- Wolfe, Dave (1982). *Propellant Profiles Volume 1*. Wolfe Publishing Company. ISBN 0-935632-10-7.

Poudre B

Poudre B single-base smokeless powder flakes

Poudre B was the first practical smokeless gunpowder . It was perfected between 1882 and 1884 at "Laboratoire Central des Poudres et Salpetres" in Paris, France. Originally called "Poudre V", from the name of the inventor, Paul Vieille, it was arbitrarily renamed "Poudre B" (short for *poudre blanche* -- white powder, as distinguished from black powder) to distract German espionage.[1] "Poudre B" is made from 68.2% insoluble nitrocellulose, 29.8% soluble nitrocellusose gelatinized with ether and 2% paraffin. "Poudre B" is made up of very small paper-thin flakes that are not white but dark greenish grey in color. "Poudre B" was first used to load the 8mm Lebel cartridges issued in 1886 for the Lebel rifle.

[] History

French chemist Paul Vieille had followed the findings of German-Swiss chemist Christian Friedrich Schonbein, who had created the explosive nitrocellulose or "guncotton" in 1846 by treating cotton fibers with a nitric acid and sulphuric acid mixture. However guncotton, an explosive substance, proved to be too fast burning at the time for direct use in firearms and artillery ammunition. Then Paul Vieille went one step further in 1882-84 and, after many trials and errors, succeeded in transforming guncotton into a colloidal substance by gelatinizing it in an alcohol-ether mixture following which he stabilized it with amyl alcohol. He then used roller presses to transform this gelatinized colloidal substance into extremely thin sheets which, after drying, were cut up into small flakes. This single-base smokeless powder was originally named "Poudre V " after the inventor's name . That denomination was later changed arbitrarily to "Poudre B" in order to distract German espionage. The original "Poudre B" of 1884 was almost immediately replaced by improved "Poudre BF(NT)" in 1888. In 1896 "Poudre BF(NT)" was replaced by "Poudre BF(AM)" which was followed by "Poudre BN3F" in 1901. The latter was stabilized with the antioxidant diphenylamine instead of amyl alcohol and it gave safe and regular performance as the standard French gunpowder used during World War I (1914–1918). It was followed during the 1920s by

"Poudre BN3F(Ae)" and later by "Poudre BPF1", which remained in service until the 1960s.

[] Performance

Three times more powerful than black powder for the same weight, and not generating large quantities of smoke, "Poudre B" gave the user a huge tactical advantage. It was hastily adopted by the French military in 1886, followed by all the major military powers within a few years.

Prior to its introduction, a squad of soldiers firing volleys would be unable to see their targets after a few shots, while their own location would be obvious because of the cloud of smoke hanging over them. The higher power of the new powder gave a higher muzzle velocity, which in turn produced a flatter bullet trajectory and thus a longer range. It also required lesser volumes of gunpowder and allowed a smaller caliber, thus lighter bullets, so a soldier could carry more ammunition. The French Army quickly introduced a new rifle, the Lebel Model 1886 firing a new 8 mm calibre cartridge, to exploit these benefits.

[] Stability and safety

The earliest "Poudre B" tended to eventually become unstable, which has been attributed to evaporation of the volatile solvents, but may also have been due to the difficulty in fully removing the acids used to make guncotton. In the early years of their use both the original Poudre B and guncotton led to accidents. For example, two French battleships, the *Iéna* and the *Liberté*, blew up in Toulon harbour in 1907 and 1911 respectively with heavy loss of life. By the end of the 1890s, safer smokeless powders had been developed, including improved and stabilized versions of "Poudre B" (e.g. Poudres BN3F and BPF1), ballistite and cordite. The guncotton problem is not completely solved even today, as an occasional batch of smokeless powder will still deteriorate, although this is extremely rare.

Ballistite

Ballistite is a smokeless propellant made from two high explosives, nitrocellulose and nitroglycerine. It was developed and patented by Alfred Nobel in the late 19th century.

Development of smokeless powders

For about a thousand years gunpowder, or black powder (Poudre N, *Poudre Noire*), as it was also known, was the only practical propellant. However, there were several major tactical disadvantages in the use of black powder. Firstly, a squad of soldiers firing volleys would be completely unable to see their targets after a few shots. Secondly, their location would quickly be obvious because of the huge cloud of white smoke hanging over them. Similarly, black powder severely fouled barrels, necessitating constant cleaning, sometimes in the middle of action. Such fouling also limited the introduction of rifled firearms, with their closer-fitting bullets. For rifles, this problem was partially overcome with the introduction of the Minie ball and the resulting rifled musket. Black powder fouling meant that early revolvers were often built with a relatively loose fit to prevent them from jamming. Further, autoloading firearms quickly become inoperable due to fouling. Black powder is also corrosive.

In 1884, a French chemist, Paul Vieille invented the first smokeless powder, called Poudre B (*Poudre Blanche* = white powder).[1][2] It was a great improvement over black powder. Poudre B was made from two forms of nitrocellulose (collodion and guncotton), softened with ethanol and ether, and kneaded together. It was three times more powerful than black powder and it did not generate vast quantities of smoke.[1] Smokeless powders are smokeless because their combustion products are mainly gaseous, compared to around 60% solid products for black powder, i.e. (potassium carbonate, potassium sulfate, etc.). Poudre B was therefore immediately adopted by the French military; but it tended to become unstable over time, as the volatile solvents evaporated, and this led to many accidents. For example, two battleships, the *IÃ©na* and the *LibertÃ©* blew up in Toulon harbour in 1907 and 1911, respectively.[3]

[] Military adoption of ballistite

Alfred Nobel patented ballistite in 1887 whilst he was living in Paris. His formulation was composed of 10% camphor and equal parts of nitroglycerine and collodion.[4] The camphor reacted with any acidic products of the chemical breakdown of the two explosives. This both stabilized the explosive against further decomposition and prevented spontaneous explosions. However, camphor tends to evaporate over time, leaving a potentially unstable mixture.[5]

Nobel's patent specified that the nitrocellulose should be "of the well-known soluble kind". He offered to sell the rights to the new explosive to the French government, but they declined, largely because they had just adopted Poudre B. He subsequently licensed the rights to the Italian government, who entered into a contract, on 1 August 1889, to obtain 300,000 kilogram of ballistite; and Nobel opened a factory at Avigliana, Turin.[6]

The Italian Army swiftly replaced their M1870 and M1870/87 rifles, which used black powder cartridges, to a new model, the M1890 Vetterli, which used a cartridge loaded with Ballistite.

As Italy was a competing Great Power to France, this was not received well by the French press and the public. The newspapers accused Nobel of industrial espionage, by spying on Vieille, and "high treason against France". Following a police investigation he was refused permission to conduct any more research, or to manufacture explosives in France. He therefore moved to San Remo in Italy, in 1891, where he spent the last five years of his life.[7]

[] Patent infringement claim against Great Britain

Meanwhile, a government committee in Great Britain, called the "Explosives Committee" and chaired by Sir Frederick Abel monitored foreign developments in explosives. Abel and Sir James Dewar, who was also on the committee, jointly patented a modified form of ballistite in 1889. This consisted of 58% nitroglycerin by weight, 37% guncotton and 5% petroleum jelly. Using acetone as a solvent, it was extruded as spaghetti-like rods initially called "cord powder" or "the Committee's modification of Ballistite", but this was soon abbreviated to cordite.

After unsuccessful negotiations, in 1893 Nobel sued Abel and Dewar over patent infringement and lost the case.[8] It then went to the Court of Appeal and the House of Lords in 1895 but he also lost the two appeals and the Nobel's Explosives Company had to pay the costs.[8] The claim was lost because the words "of the well-known soluble kind" in his patent were taken to mean soluble collodion, and to specifically exclude the water-insoluble guncotton.[8]

Cordite, ballistite and Poudre B continued to be used in various armed forces for many years, but cordite gradually became predominant.

Ballistite is still manufactured as a solid fuel rocket propellant, although the less volatile but chemically similar diphenylamine is used instead of camphor.

References

1. ^ *a* *b* Davis 1943, pp. 292â€“293
2. ^ SchÃ¼ck H. and Sohlman, R. (1929). *The Life of Alfred Nobel*. London: William Heinemann Ltd.
3. ^ Davis 1943, pp. 307â€“308
4. ^ SchÅ±ck & Sohlman 1929, p. 136
5. ^ SchÅ±ck & Sohlman 1929, pp. 140â€“141
6. ^ SchÅ±ck & Sohlman 1929, pp. 138â€“9
7. ^ SchÅ±ck & Sohlman 1929, pp. 139â€“140
8. ^ *a* *b* *c* SchÃ¼ck & Sohlman, page 142

Sources

- Davis, Tenney L (1943). *The Chemistry of Powder and Explosives* **II**. New York: John Wiley & Sons, Inc.
- SchÅ±ck, H; Sohlman, R (1929). *The Life of Alfred Nobel*. London: William Heinemann Ltd.

Clostridium acetobutylicum

Chaim Weizmann

Clostridium acetobutylicum, ATCC 824, is a commercially valuable bacterium sometimes called the "**Weizmann Organism**", after Jewish-Russian born Chaim Weizmann, then senior lecturer at the University of Manchester, England, used them in 1916 as a bio-chemical tool to produce at the same time, jointly, acetone, ethanol, and butanol from starch. The method was described since as the ABE process, (Acetone Butanol Ethanol fermentation process), yielding 3 parts of acetone, 6 of butanol and 1 of ethanol, reducing the former difficulties to make cordite, an explosive, from acetone and paving the way also, for instance, to obtain vehicle fuels and synthetic rubber.

Unlike yeast, which can digest sugar only into alcohol and carbon dioxide, *C. acetobutylicum* and other Clostridia can digest whey, sugar, starch, cellulose and perhaps certain types of lignin, yielding butanol, propionic acid, ether, and glycerin.

In genetic engineering

James Liao, a chemical engineer at the University of California, Los Angeles developed a method to insert genes responsible for production of butanol from *Clostridium acetobutylicum* into the bacterium *Escherichia coli*.[1][2]

References

1. ^ http://www.technologyreview.com/energy/20073
2. ^ http://www.nature.com/nature/journal/v451/n7174/pdf/nature06450.pdf

- http://www.encyclopedia.com/topic/Chaim_Weizmann.aspx
- Jones, DT; Woods, DR (1986). "Acetone-butanol fermentation revisited". *Microbiological reviews* **50** (4): 484–524. PMC 373084. PMID 3540574.Pages 484 - 524.
- Ronald M. Atlas, Richard Barta, *Microbial Ecology, Fundamentals and Applications*, Benjamin/Cummings Publishing Co. Inc., Redwood City, CA, 3rd edition, 563 pages.ISBN 0-8053-0653-6
- *Microbial Processes: Promising Technologies for Developing Countries*, National Academy of Sciences, Washington, (1979).

See,Internet: http://www.nap.edu/openbook.php?record_id=9544&page=R1. Probably, you can see, for immediate results, (consulted May 2011): 27 hits 6 Fuel and Energy 107-123 42 hits 7 Waste Treatment and Utilization 124-141 36 hits 8 Cellulose Conversion 142-157

- *UCLA researchers engineer E. coli to produce record-setting amounts of alternative fuel*, 16 March 2011, http://www.democraticunderground.com/discuss/duboard.phpaz=view_all&address=115x280888

[] Further reading

- Nölling J, Breton G, Omelchenko MV et al. (August 2001). "Genome sequence and comparative analysis of the solvent-producing bacterium Clostridium acetobutylicum". *J. Bacteriol.* **183** (16): 4823–38. doi:10.1128/JB.183.16.4823-4838.2001. PMC 99537. PMID 11466286.
- Driessen AJ, Ubbink-Kok T, Konings WN (February 1988). "Amino acid transport by membrane vesicles of an obligate anaerobic bacterium, Clostridium acetobutylicum". *J. Bacteriol.* **170** (2): 817–20. PMC 210727. PMID 2828326.
- Zappe H, Jones WA, Jones DT, Woods DR (May 1988). "Structure of an endo-beta-1,4-glucanase gene from Clostridium acetobutylicum P262 showing homology with endoglucanase genes from Bacillus spp". *Appl. Environ. Microbiol.* **54** (5): 1289–92. PMC 202643. PMID 3389820.
- Bowles LK, Ellefson WL (November 1985). "Effects of butanol on Clostridium acetobutylicum". *Appl. Environ. Microbiol.* **50** (5): 1165–70. PMC 238718. PMID 2868690.

[] External links

- ATCC reference organism 824 C.Acetobutylicum.
- findarticles.com: Bacteria speeds drug to tumors - use of Clostridium acetobutylicum enzyme to activate cancer drug CB 1954.
- EPA Clostridium acetobutylicum Final Risk Assessment
- Carolina Bio Supply Living Culture Order Page
- Genetic Engineering of Clostridium acetobutylicum for Enhanced Production of Hydrogen Gas: Penn State University.
- Pathema-*Clostridium* Resource
- US Patent 1,875,536, issued September, 1932, Wheeler et al.
- US Patent 1,315,585, issued September, 1919, Weizmann
- Applied Microbiology and Biotechnology, Volume 87, Issue 4, July 2010, Pages 1303-1315, 129 references, *Trends and challenges in the microbial production of lignocellulosic bioalcohol fuels* by Weber, C., Farwick, A., Benisch, F., Brat, D., Dietz, H., Subtil, T., Boles, Institute of Molecular Biosciences, Goethe-University Frankfurt Am Main, Max-von-Laue-Str. 9, Frankfurt am Main 60438, Germany. Cited only 4 times, (????), by others according to Computer searches made on 17 May 2011.

ISSN: 01757598 CODEN: AMBID doi:10.1007/s00253-010-2707-z PMID 20535464
Document Type: Short Survey Source Type: Journal

Acetone-butanol-ethanol fermentation

Acetone-butanol-ethanol (ABE) fermentation is a process that uses bacterial Fermentation to produce acetone, n-Butanol, and ethanol from starch. It was developed by the chemist Chaim Weizmann and was the primary process used to make acetone during World War I, such as to produce cordite. The process is anaerobic (done in the absence of oxygen), similar to how yeast ferments sugars to produce ethanol for wine, beer, or fuel. The process produces these solvents in a ratio of 3-6-1, or 3 parts acetone, 6 parts butanol and 1 part ethanol. It usually uses a strain of bacteria from the Clostridia Class (Clostridium Family). Clostridium acetobutylicum is the most well-known strain, although Clostridium beijerinckii has also been used for this process with good results.

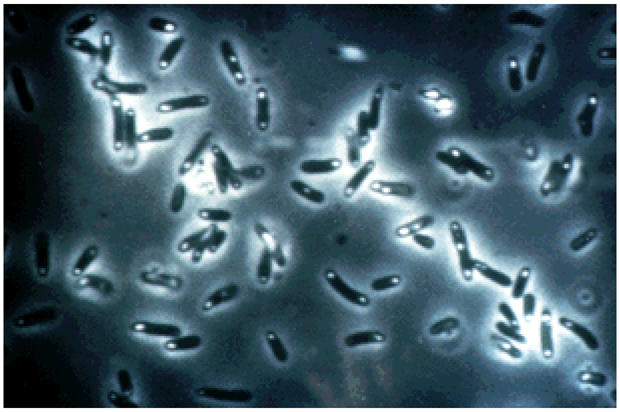
The production of butanol by biological means was first performed by Louis Pasteur in 1861. In 1905, Schardinger found that acetone could similarly be produced. Fernbach's work of 1911 involved the use of potato starch as a feedstock in the production of butanol. Industrial exploitation of ABE fermentation started in 1916 with Chaim Weizmann's isolation of Clostridium acetobutylicum, as described in U.S. patent 1315585.

In order to make ABE fermentation profitable, many in-situ product recovery systems have been developed. These include gas stripping, pervaporation, membrane extraction, adsorption, and reverse osmosis. However, at this time none of them have been implemented at an industrial scale.

For gas stripping, the most common gases used are the off-gases from the fermentation itself, a mixture of carbon dioxide and hydrogen gas.

ABE fermentation, however, is not profitable when compared to the production of these solvents from petroleum. As such there are no currently operating ABE plants. During the 1950s and 1960s, ABE fermentation was replaced by petroleum chemical plants. Due to different raw materials costs, ABE fermentation was viable in South Africa until the early 1980s, with the last plant closing in 1983.

Microbial Fermentations: Changed The Course Of Human History



Localized protein deposits inside rod-shape E. coli bacteria(X2000).
by Genentech, Corporate Communication

Christine Case, Ed.D.
Microbiology Professor, Skyline College

When people find out that I'm a microbiologist they frequently ask how I live: "Is your house scrupulously clean? Do you sterilize everything? How do you avoid microbes?" Undaunted by questions concerning my house-cleaning, I enjoy providing examples of the importance of microorganisms in our daily lives and the myriad of foods and drugs that microbes produce. I know that microbiological discoveries have played an important part in the course of human history, contributing to advances in health, nutrition, and use of environmental resources. I was captivated and amazed, however, to learn that microbiology was instrumental in the origination of an entire country and that a microbiologist was elected a nation's president.

My training and research experience is in industrial microbiology, where microorganisms are put to work to make a product. Fermentation is an important part of industrial microbiology. Fermentation technology got its origins the first time someone made wine, was perfected in the 1940's with the production of antibiotics, and is the now the primary method of production in the biotechnology industry.

What Is Fermentation?

Fermentation has always been an important part of our lives: foods can be spoiled by microbial fermentations, foods can be made by microbial fermentations, and muscle cells use fermentation to provide us with quick responses. Fermentation could be called the staff of life because it gives us the basic food, bread. But how fermentation actually works was not understood until the work of Louis Pasteur in the latter part of the nineteenth century and the research which followed.

Fermentation is the process that produces alcoholic beverages or acidic dairy products. For a cell, fermentation is a way of getting energy without using oxygen. In general, fermentation involves the breaking down of complex organic substances into simpler ones. The microbial or animal cell obtains energy through glycolysis, splitting a sugar molecule and removing electrons from the molecule. The electrons are then passed to an organic molecule such as pyruvic acid. This results in the formation of a waste product that is excreted from the cell. Waste products formed in this way include ethyl alcohol, butyl alcohol, lactic acid, and acetone--the substances vital to our utilization of fermentation.

Lactic Acid Fermentation

During lactic acid fermentation, the electrons released during glycolysis are passed to pyruvic acid to form two molecules of lactic acid. Lactic acid fermentation is carried out by many bacteria, most notably by the lactic acid bacteria used in the production of yogurt, cheese, sauerkraut, and pickles. Some animal cells such as muscle cells can also use fermentation for a quick burst of energy.

Alcohol Fermentation

Alcohol fermentation also begins with glycolysis to produce two molecules of pyruvic acid, two molecules of ATP, and four electrons. Each pyruvic acid is modified to acetaldehyde and CO2. Two molecules of ethyl alcohol are formed when each acetaldehyde molecule accepts two electrons. Alcohol fermentation is carried out by many bacteria and yeasts .

Fermentation in Industry

In industry, as well as other areas, the uses of fermentation progressed rapidly after Pasteur's discoveries. Between 1900 and 1930, ethyl alcohol and butyl alcohol were the most important industrial fermentations in the world. But by the 1960s, chemical synthesis of alcohols and other solvents were less expensive and interest in fermentations waned. Questions can be raised about chemical synthesis, however. Chemical manufacture of organic molecules such as alcohols and acetone rely on starting materials made from petroleum. Petroleum is a nonrenewable resource; dependence on such resources could be considered short-sighted. Additionally, the use of petroleum has concomitant environmental and political problems.

Interest in microbial fermentations is experiencing a renaissance. In 1995, J. W. Frost and K. M. Draths wrote that "chemistry is moving into a new era" in which renewable resources and microbial biocatalysts will be prominent. Plant starch, cellulose from agricultural waste, and whey from cheese manufacture are abundant and renewable sources of fermentable carbohydrates. Additionally these materials, not utilized, represent solid waste that must be buried in dumps or treated with waste water.

Microbial fermentations have other benefits. For one, they don't use toxic reagents or require the addition of intermediate reagents. Microbiologists are now looking for naturally occurring microbes that produce desired chemicals. In addition, they are now capable of engineering microbes to enhance production of these chemicals. In recent years, microbial fermentations have been revolutionized by the application of genetically-engineered organisms. Many fermentations use bacteria but a growing number involve culturing mammalian cells. Some examples of products currently produced by fermentation are listed in Tables 1 and 2 .

How Does Fermentation Work in Biotechnology?

In the pharmaceutical and biotechnology industries, fermentation is any large-scale cultivation of microbes or other single cells, occurring with or without air. In the teaching lab or at the research bench, fermentation is often demonstrated in a test tube, flask, or bottle-in volumes from a few milliliters to two liters. At the production and manufacturing level, large vessels called fermenters or bioreactors are used. A bioreactor may hold several liters to several thousand liters. Bioreactors are equipped with aeration devices as well as nutrients, stirrers, and pH and temperature controls.

At Genentech, Inc., for example, in order to get a product from fermentation, fermentation scientists develop media and test growth conditions. Then, a scale-up must be done to reproduce the process at a large volume. During production, technicians monitor temperature, pH, and growth in the bioreactors to ensure that conditions are optimum for cell growth and product. Bioreactors are used to make products such as insulin and human growth hormone from genetically engineered microorganisms as well as products from naturally-occurring cells, such as the food additive xanthan.

The products being developed by the biotechnology industry have enormous implications for our future health and well-being. All of the exciting discoveries in current biotechnical research and its applications will, of course, have repercussions within human history. Science and politics have always interacted, in both direct and indirect ways.

Microbiology, Synthetic Rubber, and The Making of a Nation

The uses for rubber were limited until 1898 when John Dunlop used vulcanized (heated or fireproofed) rubber to make automobile tires. The rest, as they say, is history: By 1918, there were more than nine million cars in the United States and the United States was using 50 percent of the world's rubber production. Already, by around 1900, the growing demand for rubber and the desire by countries to be self-sufficient motivated scientists to develop synthetic rubber. The greatest stimulus for development of synthetic rubber, however, was the blockade of Germany during World War I. Faced with a cutoff of its supply of natural rubber, Germany succeeded in manufacturing synthetic rubber by polymerizing butadiene, which is obtained from petroleum or alcohol.

In 1904, Chaim Weizmann was a chemistry professor at Manchester University in England trying to make synthetic rubber. He was looking for a microbe that would produce the necessary butyl alcohol. Weizmann was a Russian-born Jew who was active in the Zionist movement which advocated the creation of a homeland for Jews in Palestine. During his stay in England, he became a leader of the international Zionist movement.

By 1914, Weizmann had isolated *Clostridium acetobutylicum,* a bacterium which used inexpensive starch to produce a high yield of butyl alcohol and acetone. However, World War I broke out in August of 1914 and diverted attention away from synthetic rubber and toward gunpowder (cordite). As it turns out, the solvent for making nitrocellulose and thus cordite was acetone. Weizmann was instrumental in making available a source for the creation of this acetone.

Acetone had previously been made from calcium acetate imported from Germany. Since importation of the German calcium acetate was not possible and the United States did not have a large supply, Weizmann was recruited by Winston Churchill and the British government to set up his microbial fermentation for the production of acetone from corn at the Nicholson Distillery in London. The grain supply was unreliable, however, because of the German blockade and it was necessary to look for a different fermentable carbohydrate. Food was being rationed so a substrate that could not be used for human food was needed. In 1916, Weizmann even tried to use horse chestnuts collected by children, but the supply was insufficient for a large-scale fermentation. The British turned to other parts of the British Empire and to their allies for a fermentable carbohydrate. Consequently, in 1916, the Weizmann process was moved to a distillery in Toronto (Canada) and another was built in India. In 1917, a plant was set up to ferment corn in Indiana (U.S.).

After the war, when British Prime Minister Lloyd George asked what honors Weizmann might want for his considerable contributions, Weizmann answered, "There is only one thing I want. A national home for my people." Lord Balfour then gave Weizmann 15 minutes to explain why that national homeland should be Palestine. Weizmann was an eloquent spokesman and convincingly stated his case. The result was the Balfour Declaration, which affirmed Britain's commitment to the establishment of a Jewish homeland.

Weizmann went on to make significant contributions to both microbiology and politics. In 1920, he began a long tenure as President of the World Zionist Organization. In the years that followed, he campaigned with great zeal. In 1948, when the United States was going to reverse its decision to support the independent state of Israel, Weizmann used his considerable negotiating skills to convince President Truman that the United States should affirm their support for the new country, leading to the founding of Israel. In 1949, he was elected the first president of Israel.

From microbiologist to President, Weizmann illustrates not only the persistence necessary in both research and politics, but the strange and interesting ways research and politics interact. What further developments will the products of biotechnical research inspire?

Missing name for redirect.

The Horse Chestnut, and how it changed the world

In school logbooks from all over England, if you carefully look through the records for 1917 and 1918, you will find letters of thanks from the Director of Propellant Supplies for horse chestnuts gathered by schoolchildren and sent in to the local government offices.

Sadly, despite the many goey green images this manages to conjure up, there were no Chestnut Grenades used during the first world war.

In fact, according to *Chemistry in Britain* (February 1987), the Royal Society of Chemistry's monthly periodical (now superceded by the much trendier-named *Chemistry world*) and the Imperial War Museum in London, the horse chestnuts were a source of acetone, a solvent needed for the production of cordite, the exciting new 'smokeless powder' that changed firearms from battlefield smoke machines to the lean, mean widow-makers of 20th-century warfare.

65% guncotton, 30% nitroglycerine and 5% petroleum jelly, cordite had to be gelatinized before it could be packed into shells and small arms munitions, a process to which acetone was vital. However, when war broke out, there were only 3200 tons of acetone squirrelled away for military use. Previously, the only industrial method of producing acetone was the destructive distillation of wood, a market which the (rapidly decreasing) lush forests of North America pretty much had cornered. It was clear, however, that not enough acetone could be imported from the United States to meet Britain's wartime needs.

So the minister of munitions, David Lloyd George, appointed Chaim Weizmann, a chemist who had emigrated from mainland Europe in 1904, to solve the acetone problem. Weizmann had patented a process whereby acetone could be produced by fermentation of maize and potatoes, so the Poms started importing *maize* from the United States instead. The Germans, not being utter morons, launched a submarine offensive in the Pacific in 1916, and made intercontinental transport a serious problem. Stocks of maize, and of acetone, ran dangerously low.

So Weizmann, the enterprising and single-minded individual that he was, adapted his process so that horse chestnuts could be substituted, although they were far from ideal. A factory was built at King's Lynn in Norfolk specifically for processing chestnuts, and vast quantities of them were gathered by schoolchildren all over England. Of course, actually *getting* them *to* the factory was less straightforward - letters to The Times complained of huge bags of chestnuts sitting rotting at train stations.

Finally, in April 1918, the King's Lynn factory began making chestnut-derived acetone in earnest, enjoying a fruitful and pithy lifetime of 3 short months before being closed again in July 1918.

Our boy Lloyd George, however, was *ever* so grateful to Weizmann. When he was made Prime Minister he allowed Weizmann - a firm Zionist - free access to his foreign secretary, A. J. Balfour. Students of Palestinian history might recall the infamous Balfour Declaration, in which Mother England expressed complisance in "the establishment in Palestine of a national home for the Jewish people."

In fact, students of Palestinian history will probably have long ago recognised Chaim Weizmann as the first president of Israel, a position he held from 1948 until his death in 1952.

So remember, as Israel slowly conkers the Middle East: pretty and tempting they might be, but horse chestnuts really are a bitter, toxic fruit.

Did conkers help win the First World War?

When Britain's war effort was threatened by a shortage of shells, the government exhorted schoolchildren across the country to go on the hunt for horse chestnuts. Saul David, who fronts the current BBC Four series *Bullets, Boots And Bandages: How To Really Win A War*, explains why

In the autumn of 1917, a notice appeared on the walls of classrooms and scout huts across Britain: "Groups of scholars and boy scouts are being organised to collect conkers... This collection is invaluable war work and is very urgent. Please encourage it."

It was never explained to schoolchildren exactly how conkers could help the war effort. Nor did they care. They were more interested in the War Office's bounty of 7s 6d (37.5p) for every hundred weight they handed in, and for weeks they scoured woods and lanes for the shiny brown objects they usually destroyed in the playground game.

The children's efforts were so successful that they collected more conkers than there were trains to transport them, and piles were seen rotting at railway stations. But a total of 3,000 tonnes of conkers did reach their destination – the Synthetic Products Company at King's Lynn – where they were used to make acetone, a vital component of the smokeless propellant for shells and bullets known as cordite.

Cordite had been used by the British military since 1889, when it first replaced black gunpowder. It consisted chiefly of the high-explosives nitroglycerine and nitrocellulose (gun-cotton), with acetone playing the key role of solvent in the manufacturing process.

Prior to the First World War, the acetone used in British munitions was made almost entirely from the dry distillation (pyrolysis) of wood. As it required almost a hundred tonnes of birch, beech or maple to produce a tonne of acetone, the great timber-growing countries were the biggest producers of this vital commodity, and Britain was forced to import the vast majority of its acetone from the United States.

An attempt to produce our own acetone was made in 1913 when a modern factory was built in the Forest of Dean. But by the outbreak of war in 1914, the stocks for military use were just 3,200 tonnes, and it was soon obvious that an alternative domestic supply would be needed. This became even more pressing during the spring of 1915 when an acute shortage of shells – the so-called 'shell crisis' – reduced some British guns to firing just four times a day.

The British government's response was to create a dedicated Ministry of Munitions, run by the future prime minister David Lloyd George. One of Lloyd George's first initiatives was to ask the brilliant chemist Chaim Weizmann of Manchester University if there was an alternative way of making acetone in large quantities. Weizmann said yes.

Developing the work of Louis Pasteur and others, Weizmann had perfected an anaerobic fermentation process that used a highly vigorous bacterium known as Clostridium acetobutylicum (also known as the Weizmann organism) to produce large quantities of acetone from a variety of starchy foodstuffs such as grain, maize and rice. He at once agreed to place his process at the disposal of the government.

In May 1915, after Weizmann had demonstrated to the Admiralty that he could convert 100 tonnes of grain to 12 tonnes of acetone, the government commandeered brewing and distillery equipment, and built factories to utilise the new process at Holton Heath in Dorset and King's Lynn in Norfolk. Together they produced more than 90,000 gallons of acetone a year, enough to feed the war's seemingly insatiable demand for cordite. (The British army and Royal Navy, alone, fired 248 million shells from 1914 to 1918.)

But by 1917, as grain and potatoes were needed to feed the British population, and German U-boat activity in the Atlantic was threatening to cut off the import of maize from the United States, Weizmann was tasked to find another supply of starch for his process that would not interfere with the already limited food supplies.

He began experimenting with conkers, aware that they grew in abundance across the country, and found that the yield of acetone was sufficiently high to begin production. This, in turn, prompted the nationwide appeal for schoolchildren to collect the conkers and hand them in.

The government was determined not to reveal the real reason for the great chestnut hunt of 1917 in case the blockaded Germans copied their methods. The only official statement was printed in The Times on 26 July 1917.

It read: "Chestnut seeds, not the green husks, are required by the Government for the Ministry of Munitions. The nuts will replace cereals which have been necessary for the production of an article of great importance in the prosecution of the War."

When questions were asked in the House of Commons, the veiled response was that the conkers were needed for "certain purposes". So suspicious did some members of the public become that they accused the government of using voluntary labour for private profit.

The actual production of acetone from conkers was, despite Weizmann's assurances, never that successful. Teething problems meant the manufacturing process did not begin in the King's Lynn factory until April 1918, and it was soon discovered that horse chestnuts did not provide the yields the government had hoped for. Production ended after just three months.

So did conkers really help to win the war? They played their part, certainly, even if their role was more walk-on than centre stage. The real star of the show was Chaim Weizmann, whose brilliant solution to the acetone shortage – using a variety of natural products from maize to conkers – helped to solve the shell crisis and get Britain's guns firing again.

A leading Zionist, Weizmann was rewarded for his vital contribution to Britain's war effort when the cabinet – prompted by Lloyd George, prime minister since late 1916 – approved the signing of the Balfour Declaration on 2 November 1917. Taking the form of a letter from Arthur Balfour, the foreign secretary, to Lord Rothschild, a leading British Jew, it promised government support "for the establishment in Palestine of a national home for the Jewish people", and was the first step on the long road to Israeli statehood.

When the state of Israel was finally established in 1948, Weizmann became its first president. For good or ill, conkers were partly responsible.

Fortune favours the well prepared, well-mannered, and hard-working

May 10, 2011

How British horse chestnuts influenced the foundation of Israel.

There is a *tale* of a British politician in WWI who had a policy of having tea with a wide range of people, and one day had tea with a White Russian (refugee from destruction of Czarist Russia) Jew. It happened that conversation turned to the problems of the military, as their main source of acetone - an ingredient in cordite for munitions – was lost through the war. The refugee said " I can help you there – I have a way to make acetone from horse-chestnuts" . The government invested in his method, and was able to make the shells needed to continue the war. Later, grateful for his assistance, the British listened to his arguments in support of the creation of Israel.

This sounds like chance favouring the politician who was willing to meet odd people and listened to a refugee grumble , and the refugee who met the politician – but the reality is more complex. The politician was Lloyd George, the “refugee” was Chaim Weizmann.

According to Wikipedia, “Weizmann studied chemistry at the Polytechnic Institute of Darmstadt, Germany, and University of Freiburg, Switzerland. In 1899, he was awarded a doctorate with honors. In 1901, he was appointed assistant lecturer at the University of Geneva and, in 1904, senior lecturer at the University of Manchester.”

Weizmann had become interested in the bacteriology of fermentation, and sent many years testing cultures for the ability to produce useful chemicals like butyl alcohol from fermenting maize. This was complicated by commercial restrictions on other scientists sharing processes and cultures. One of his cultures (later named ‘Clostridium aceto-butylicum Weizmann’) produced good amounts of butyl alcohol, but also fair amounts of acetone.

At the same time, he was strongly involved in the more militant branch of Zionism, weary of centuries of racism. He was invited to tea with a middle-class, well-assimilated Jewish family, and there met another guest – a distinguished journalist. Through conversation with this gentleman he gained introductions to senior politicians, arguing for his cause.

In 1915, through a series of contacts suggested by scientific friends, and through demonstrations of the laboratory-level success of his bacillus and brewing and distillation techniques, he became one of three scientists separately funded to develop methods for manufacturing acetone. He made modest requests for immediate funding, accepting later payment in order to support the war effort, with a gentlemanly manner much appreciated by the Government. He rapidly scaled up the process from kilogram to tonne output, and found ways to ferment carbohydrate sources other than maize.

The other two methods proved less successful, and, with the strict rationing required later in WWI, the ability to ferment horse-chestnuts was a strong factor in Weizmann’s popularity: children would collect the nuts for shipping to the factory, “helping the war effort.” Thus,the Government’s willingness to support early-stage science paid off, even though two in three did not pan out. They prepared for later needs by seeking out appropriate science, were courteous in dealing with the scientists, and dealt with the bureaucratic labour involved – so fortune later favoured them.

And Weizmann? From a great deal of hard work, a gentlemanly approach, and knowing influential people on more than a scientific basis; with a good public profile and with the British Government in his (moral) debt, as the head of the British Zionist Federation and later the World Zionist Organisation he dealt with British (and other) politicians. This took up a great deal of his time between the wars (WWI and WWII), while he continued his research, industrial production of fermentation products, and development of what became the Weizmann Institute of Science in what became Israel.

Weizmann became the first President of the new state of Israel in 1949.

Fortune favoured the well-prepared, well-mannered, and hard-working.

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This blog entry was made possible through talking with a friend who watched a documentary on the Atlantic, through Wikipedia, and through my paying an annual fee to have access, through a University library, to online versions of journal articles. In this case, particularly to J. Reinharz (1985) Science in the service of politics:the case of Chaim Weizmann during the First World War. *English Historical Review* Vol. 100, No. 396 (Jul., 1985): 572-603. doi: 10.1093/ehr/C.CCCXCVI.572: . This is worth reading in its entirety.

The title derives from *“Dans les champs de l’observation le hasard ne favorise que les esprits préparés.”* (**In the fields of observation chance favoors only the prepared mind)** : Louis Pasteur, Lecture, University of Lille (7 December 1854).
http://en.wikiquote.org/wiki/Louis_Pasteur

Aesculus hippocastanum

Aesculus hippocastanum

Aesculus hippocastanum, Horse-chestnut planted as a feature tree in a park

Distribution

Aesculus hippocastanum is native to a small area in the Pindus Mountains mixed forests and Balkan mixed forests of South East Europe.[1] It is widely cultivated in streets and parks throughout the temperate world.

[] Growth

A. hippocastanum grows to 36 metres (118 ft) tall, with a domed crown of stout branches; on old trees the outer branches often pendulous with curled-up tips. The leaves are opposite and palmately compound, with 5–7 leaflets; each leaflet is 13–30 cm long, making the whole leaf up to 60 cm across, with a 7–20 cm petiole. The leaf scars left on twigs after the leaves have fallen have a distinctive horseshoe shape, complete with seven "nails". The flowers are usually white with a small red spot; they are produced in spring in erect panicles 10–30 cm tall with about 20–50 flowers on each panicle. Usually only 1–5 fruit develop on each panicle; the shell is a green, spiky capsule containing one (rarely two or three) nut-like seeds called conkers or horse-chestnuts. Each conker is 2–4 cm diameter, glossy nut-brown with a whitish scar at the base.[2]

[] Etymology

The common name "horse-chestnut" (often unhyphenated) is reported as having originated from the erroneous belief that the tree was a kind of chestnut (though in fact only distantly related), together with the observation that eating the fruit cured horses of chest complaints[3] despite this plant being poisonous to horses.

[] Uses

Cultivation for its spectacular spring flowers is successful in a wide range of temperate climatic conditions provided summers are not too hot, with trees being grown as far north as Edmonton, Alberta, Canada,[4] the Faroe Islands,[5] and Harstad, Norway.

This tree[6] and the red flowering cultivar *A. hippocastanum* 'Baumannii'[7] have gained the Royal Horticultural Society's Award of Garden Merit.

In Britain and Ireland, the nuts are used for the popular children's game conkers. During the two world wars, horse-chestnuts were used as a source of starch which in turn could be fermented via the *Clostridium acetobutylicum* method devised by Chaim Weizmann to produce acetone. This acetone was then used as a solvent which aided in the process of ballistite extrusion into cordite, which was then used in military armaments.

A selection of fresh conkers from a horse-chestnut

The nuts, especially those that are young and fresh, are slightly poisonous, containing alkaloid saponins and glucosides. Although not dangerous to touch, they cause sickness when eaten; consumed by horses, they can cause tremors and lack of coordination.[8] Some mammals, notably deer, are able to break down the toxins and eat them safely.[*citation needed*]

In the past, horse-chestnut seeds were used in France and Switzerland for whitening hemp, flax, silk and wool. They contain a soapy juice, fit for washing of linens and stuffs, for milling of caps and stockings, etc., and for fulling of cloth. For this, 20 horse-chestnut seeds were sufficient for six litres of water. They were peeled, then rasped or dried, and ground in a malt or other mill. The water must be soft, either rain or river water; hard well water will not work. The nuts are then steeped in cold water, which soon becomes frothy, as with soap, and then turns milky white. The liquid must be stirred well at first, and then, after standing to settle, strained or poured off clear. Linen washed in this liquid, and afterwards rinsed in clear running water, takes on an agreeable light sky-blue colour. It takes spots out of both linen and wool, and never damages or injures the cloth.

In Bavaria the chestnut[*clarification needed*] is the typical tree for a beer garden. Originally they were planted for their deep shade which meant that beer cellar owners could cut ice from local rivers and lakes in winter to cool the Märzen Lager beer well into summer. Nowadays guests enjoy the shade to keep their heads cool.

Horse-chestnuts have been threatened by the leaf-mining moth *Cameraria ohridella*, whose larvae feed on horse chestnut leaves. The moth was described from Macedonia where the species was discovered in 1984 but took 18 years to reach Britain.[9]

The flower is the symbol of the city of Kiev, capital of Ukraine.[10] Although the horse-chestnut is sometimes known as the buckeye, this name is generally reserved for the New World members of the *Aesculus* genus.

[] Medicinal uses

The seed extract standardized to around 20 percent aescin (escin) is used for its venotonic effect, vascular protection, anti-inflammatory and free radical scavenging properties.[11] [12] Primary indication is chronic venous insufficiency.[13] [12]A recent Cochrane Review found the evidence suggests that Horse Chestnut Seed Extract is an efficacious and safe short-term treatment for chronic venous insufficiency.[14]

Aescin reduces fluid leaks to surrounding tissue by reducing both the number and size of membrane pores in the veins.[*medical citation needed*]

Commonly used dose: Oral use, 250-300 mg extract standardized to around 20 percent aescin 1-3 times a day. Topical as a cream with 2% aescin.

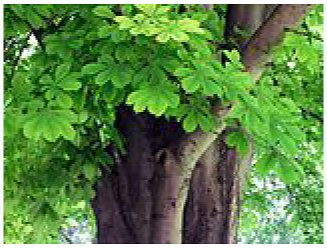
Based on reports of worsening kidney function in people with kidney disease who received intravenous aescin, it is contraindicated in kidney and liver disease. Consistently very large oral doses should be avoided.

Raw Horse Chestnut seed, leaf, bark and flower are toxic due to the presence of esculin and should not be ingested. Horse chestnut seed is classified by the FDA as an unsafe herb.[12] The glycoside and saponin constituents are considered toxic.[12]

Aesculus hippocastanum is used in Bach flower remedies. When the buds are used it is referred to as "chestnut bud" and when the flowers are used it is referred to as "white chestnut".

Quercetin 3,4'-diglucoside, a flavonol glycoside can also be found in horse chestnut seeds.[15]

Gallery

- 

Leaves and trunk

- 

Foliage and flowers

- 

Close-up of flowers

- 

Trunk

- 

Germination on lawn

1. **Horse Chestnut Powder**

1 oz Net Wt [$2.00]

2 oz Net Wt [$3.80]

4 oz Net Wt [$7.20]

8 oz Net Wt [$13.60]

16 oz Net Wt - 1 lb [$25.60]

32 oz Net Wt - 2 lbs [$48.00]

80 oz Net Wt - 5 lbs [$112.00

Description

Technical Specifications

Formulation and Usage Information

Horse Chestnut (Aesculus hippocastanum) is a large deciduous tree that is native to a small area in the mountains of the Balkans in southeast Europe, in small areas in northern Greece, Albania, the Republic of Macedonia, Serbia, and Bulgaria. It is widely cultivated throughout the temperate world.

It grows to 36 m tall, with a domed crown of stout branches, on old trees the outer branches often pendulous with curled-up tips. The flowers are usually white with a small red spot; they are produced in spring in erect panicles 10-30 cm tall with about 20-50 flowers on each panicle. Usually only 1-5 fruit develop on each panicle; the fruit is a green, softly spiky capsule containing one (rarely two or three) nut-like seeds called conkers or horse-chestnuts. Each conker is 2-4 cm diameter, glossy nut-brown with a whitish scar at the base.

The name is very often given as just 'Horse-chestnut' or 'Horse Chestnut'; the addition of 'Common' to the name however helps distinguish it from other species of horse-chestnut.

During the two world wars, horse-chestnuts were used as a source of starch which in turn could be used via the Clostridium acetobutylicum fermentation method devised by Chaim Weizmann to produce acetone. This acetone was then used as a solvent which aided in the process of ballistite extrusion into cordite, which was then used in military armaments.

The nuts, especially those that are young and fresh, are slightly poisonous, containing alkaloid saponins and glucosides. Although not dangerous to touch, they cause sickness when eaten. Some mammals, notably deer, are able to break down the toxins and eat them safely. They are reputed to be good for horses with wind, but this is unproven and feeding them to horses is not advisable. The saponin aescin, however, has been used for health purposes (such as varicose veins, edema, sprains) and is available in food supplements, as is a related glocoside aesculin.

In the past, Horse-chestnut seeds were used in France and Switzerland for whitening hemp, flax, silk and wool. They contain a soapy juice, fit for washing of linens and stuffs, for milling of caps and stockings, etc., and for fulling of cloth. For this, 20 horse-chestnut seeds were sufficient for six liters of water. They were peeled, then rasped or dried, and ground in a malt or other mill. The water must be soft, either rain or river water; hard well water will not work. The nuts are then steeped in cold water, which soon becomes frothy, as with soap, and then turns milky white. The liquid must be stirred well at first, and then, after standing to settle, strained or poured off clear. Linen washed in this liquid, and afterwards rinsed in clear running water, takes on an agreeable light sky-blue color. It takes spots out of both linen and wool, and never damages or injures the cloth.

Horse-chestnuts can be used to make jewelry using the conkers as beads. The Horse-chestnut, like some of the other members of the Aesculus genus, can also be known as buckeye, though this term is usually reserved for the New World species.

Fermentation

- Many possible paths
- 4 highlights
- THEME: all eventually oxidize NADH to NAD+
- Important to US
    - Whole variety of industrial products from this
    - Can be used to identify bacteria bc a given pathway is unique to a particular group of microorganisms
    - Identify by fermentation pattern
    - Specific examples:

Lactic acid fermentation

- One step: pyruvate (relatively more oxidized) makes lactic acid
- NADH reduced to NAD+
- Pyruvate is the organic molecule that is the electron acceptor (instead of something inorganic)
- Powers glycolysis
- Subtypes of lactic acid fermentation
    - Simple case shown above called **homolactic fermentation**
        - lactic acid only end product
        - Lactococcus and lactobacillus
    - **Heterolactic fermentation**
        - get lactic acid and mix of other products
        - More complicated
        - Also get acetic acid, ethanol, CO2
        - Luconostoc (?)

Ethanol fermentation

- More complicated: 2 steps
- Step 1 – start with pyruvate (3 carbon), remove carbon in form of CO2, get acid aldehyde (2 carbon)
- Step 2 – start with aldehyde (more oxidized) – reduced to ethanol (more reduced)

- 2 products: CO2 from first step and ethanol from second step
- Ethanol is a high energy, high calorie molecule
- No ATP made
- Saccharomyces (eukaryotic, most others bacterial) main genus for commercial fermentation
- Found in bacterial species

Propionic acid fermentation

- Many steps
- **End products** CO2 and propionic acid and propionate
- Bacteria involved: propiony bacterium
- Useful to us – used as food preservative
- Used in swiss cheese – naturally preserves
    - CO2 makes holes in cheese

Butanol (Buteric acid – different things) fermentation

- Pyruvate fermented in a series of reactions
- Makes a little ATP
- Get many products
    - CO2, organic acids (buteric acid), industrial solvents (butanol, acetone, isopropynol (isopropyl alcohol))
- Common among clostridium genus
- Strict anaerobes – create oxygen free conditions
- Many pathogens in this group
    - Gas gangrene – clostridium species
    - Gas is CO2
    - Occurs when wound does not receive oxygen
    - Makes gas
    - Smelly products of fermentation – buteric acid smells like vomit – acetone smells like fingernail polish – butanol smells bad
    - Can also use clostridium species to produce useful solvents (historically)
    - Example: in WWI british needed these solvents: mostly acetone, butanol (rubber)
    - Acetone essential to make cordite
    - Cordite is replacement for gun powder
    - Used in rifle cartridges, naval guns, mostly for artillery (critical). Need tons of cordite!!
    - Problem for brits in WWI- germans control supply of raw materials for acetone
    - Solution: Kaim Vitzman (Russian biochemist by birth, lives in england)
    - He can make acetone using clostridium
    - Feeds the clostridium certain starches, grains, etc
    - They ferment and make acetone

    - Among sources of starch: used horse chestnuts
    - Schoolkids collected these “conkers”
    - Helped win WWI
    - Brits grateful – wants homeland for Jews in Palestine
    - Brits control Palestine and it makes sense
    - Brits balfort declaration 1917 – one of many steps for founding state of Israel
    - After established, vitzman first president of israel
    - “prime minister” has real power. But still.

Use of fermentation in creation of fermented foods

- We WANT fermentation to occur in food
- As a result of actions of microorganisms
- Foods in which the growth of microbes will contribute
    - Flavor
    - Aroma
    - Improves storage properties (doesn’t rot as fast)
    - Add preservatives - Mostly organic acids
- Preserve bread with **sourdough bread**
    - Use yeast (makes bread rise)
    - Use lactobacillus
        - Lactobacillus adds organic acids
        - Lowers pH of bread considerably to 3.8-4.5 (makes it sour!)
        - Extends shelf life
        - Longer to spoil
    - Popular in san Francisco in late 1840s – gold rush
    - Miners want bread that won’t spoil
    - Later on, microbiologists isolated the lactobacillus that was being used in san Francisco
    - Named it lactobacillus sanfranciscincus (incus means “comes from”)
- Also ferment **vegetables**
    - General process: veggies soaked in salt water
    - Salts have several effects:
        - Pulls water from plant cells
        - HYPERtonic environment
        - When pull water out, sugars accompany
        - Water surrounding veggie has salt and sugar
        - Sugar is substrate or starting material for fermentation
        - Salts also inhibit undesirable spoilage microbes
        - We want certain microbes to grow, but not others
        - Establish conditions that will favor the desirable microbes (fermenters)
        - Encourages good bugs and gets rid of bad bugs
        - Fermentation step that adds mostly organic acids that then add certain flavors and preservatives
        - Many microbes then inhibited by two things: salts and low pH

- Some things can tolerate these conditions, but shelf life increased
- Ultimately spoiled by fungi – survive low pH
- Pickles usually start w/ cucumbers
- Cabbage to sauerkraut (preserves cabbage)
- Soy sauce – more complicated – fermentation of soy beans and some sort of grain (maybe wheat)
    - More complicated – succession of microbial species. One microbe after another does something different
    - First aspergillus (mold) adds amylase (turns starch to glucose)
    - Glucose substrate for fermentation
    - Second – lactic acid bacteria takes sugars to lactic acids
    - Finally – yeasts take sugar and create ethanol (another preservative)
    - Three step proccess creates soy sauce. Self-preserved material